



INTRODUCTION

TO THE

RARER ELEMENTS.

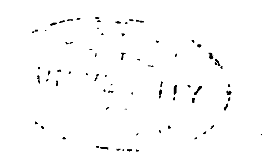
BY

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PREFACE.

This small volume, prepared from material used by the author in a short lecture course given at Yale University, is intended to serve as a convenient handbook in the introductory study of the rarer elements; that is, of those elements which are not always taken up in a general course in chemistry. No attempt has been made to treat any part of the subject exhaustively, but enough references have been given to furnish a point of departure for the student who wishes to investigate for himself. Experimental work has been included except in the case of those elements which are unavailable, either because of their scarcity or because of the difficulty of isolating them.

The author has drawn freely upon chemical journals and standard general works. In his treatment of the rare earths he has made especial use of Herzfeld and Korn's *Chemie der seltenen Erden* and Truchot's *Les Terres Rares*, works which he gladly recommends. He gratefully acknowledges the valuable assistance of his wife in preparing this material for the press.

New Haven Conn., April, 1903.

JOURNALS CITED.

American Chemical Journal.
American Journal of Science.
Analyst, The.
Annalen der Chemie und Pharmacie.
Annales de Chimie.
Annales de Chimie et de Physique.
Annalen der Physik und Chemie.
Atti della R. Accademia dei Lincei, Roma.
Berichte der Deutschen chemischen Gesellschaft.
Bulletin de l'Académie impériale de St. Pétersbourg.
Bulletin de la Société chimique de Paris.
Bulletin of the U. S. Geological Survey.
Chemisches Central-Blatt.
Chemische Industrie.
Chemical News.
Chemiker-Zeitung.
Comptes rendus de l'Académie des sciences (Paris).
Crell's Annalen.
Engineering and Mining Journal.
Jahresbericht der Chemie.
Journal of the American Chemical Society.
Journal of the London Chemical Society.
Journal of Physical Chemistry.
Journal für praktische Chemie.
Journal of the Russian Physical-Chemical Society.
Journal of the Society of Chemical Industry.
Klaproth's Beiträge.
Kongl. Vetenskaps Academiens Handlingar (Stockholm).
Liebig's Annalen der Chemie.
Monatshefte für Chemie.
Nicholson's Journal.
Philosophical Magazine.
Philosophical Transactions of the Royal Society.
Poggendorff's Annalen.
Proceedings of the American Academy of Arts and Sciences.
Proceedings of the Royal Society (London).
Rendiconto dell' Accademia delle Scienze Fisiche e Matematiche, Napoli.
Science.
Sitzungsberichte der kaiserlichen Akademie der Wissenschaften. Mathematisch-Naturwissenschaftliche Classe (Wien).
Zeitschrift für analytische Chemie.
Zeitschrift für angewandte Chemie.
Zeitschrift für anorganische Chemie.

INDEXES TO THE LITERATURE OF CERTAIN ELEMENTS.

Cæsium, Rubidium, and Lithium, Index to the Literature of; Fraprie. In preparation.

Cerium, Index to the Literature of (1751–1894); Magee. Smithsonian Misc. Coll. (1895), No. 971.

Columbium, Index to the Literature of (1801–1887); Traphagen. Smithsonian Misc. Coll. (1888), No. 663.

Didymium, Index to the Literature of (1842–1893); Langmuir. Smithsonian Misc. Coll. (1894), No. 972.

Gallium, Index to the Literature of (1876–1903);
Germanium, Index to the Literature of (1886–1903);
Indium, Index to the Literature of (1863–1903); } Browning. In preparation.

Lanthanum, Index to the Literature of (1839–1894); Magee. Smithsonian Misc. Coll. (1895), No. 971.

Lithium, *vid.* Cæsium.

Niobium or Columbium, *vid.* Columbium.

Platinum Metals, Bibliography of (1748–1897); Howe. Smithsonian Misc. Coll. (1897), No. 1084.

Rubidium, *vid.* Cæsium.

Selenium and Tellurium, Index to the Literature of; G. A. Smith. In preparation.

Tellurium, *vid.* Selenium.

Thallium, Index to the Literature of (1861–1896); Doan. Smithsonian Misc. Coll. (1899), No. 1171.

Thorium, Index to the Literature of; Joüet. Smithsonian Misc. Coll. In press.

Titanium, Index to the Literature of (1783–1876); Hallock. Annals of the N. Y. Academy of Sciences (1876), 1, 53.

Uranium, Index to the Literature of (1789–1885); Bolton. Smithsonian Report for 1885, Part 1, 915.

Vanadium, Index to the Literature of (1801–1877); Rockwell. Annals of the N. Y. Academy of Sciences (1879), 1, 133.
Yttrium Group, Index to the Literature of the Rare Earths of; Dales. In preparation.
Zirconium, Index to the Literature of (1789–1898); Langmuir and Baskerville. Smithsonian Misc. Coll. (1899), No. 1173.

Attention is called also to the following monographs:
Die Chemie des Thoriums; Koppel. Sammlung chemischer Vorträge, Band VI. Pub. by Ferd. Enke, Stuttgart, 1901.
Studien über das Tellur; Gutbier. Pub. by C. L. Hirschfeld, Leipzig, 1902.
La Chimie de L'Uranium (1872–1902); Oechsner de Coninck. Pub. by Masson et Cie., Paris, 1902.
Die analytischer Chemie des Vanadins; Valerian von Klecki. Pub. by Leopold Voss, Hamburg, 1894.

THE RARER ELEMENTS.

CÆSIUM, Cs, 133.

Discovery. Cæsium was discovered in 1860 by Bunsen and Kirchhoff while they were engaged in the spectroscopic examination of a mother-liquor from the waters of Dürkheim spring (Pogg. Annal. CXIII, 337; Chem. News II, 281). After the removal of the strontium, calcium, and magnesium, by well-known methods, and of the lithium as far as possible by ammonium carbonate, the mother-liquor was tested, and gave, in addition to the potassium, sodium, and lithium lines, two beautiful blue lines never before observed, near the strontium blue lines. Bunsen gave the name Cæsium to the newly discovered element, from the Latin *caesius*, the blue of the clear sky.

Occurrence. Cæsium is found in combination as follows:

(1) In minerals:

Pollucite, $H_2Cs_4Al_4(SiO_3)_9$, contains 31–37%* Cs_2O.

Lepidolite, $LiK(Al(OH,F)_2)\cdot Al(SiO_3)_3$, contains 0.2–0.7% Cs_2O.

Beryl, $Be_3Al_2(SiO_3)_6$, contains 0–3% Cs_2O.

(2) In certain mineral waters, among which are Dürkheim (1 liter contains about 0.21 mg. RbCl and 0.17 mg. CsCl), Nauheim, Baden-Baden, Frankenhausen, Kreuznacher, Bourbonne les Bains, Monte Catino, Wheal Clifford.

Extraction. Of the methods in use for the extraction of cæsium the following may serve as examples:

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* In the tabulation of percentages the nearest whole numbers have generally been used in this book.

(1) *From pollucite.* The finely powdered mineral is decomposed on a water-bath with strong hydrochloric acid. To the acid solution antimony trichloride is added, which precipitates the double chloride of antimony and cæsium ($3CsCl \cdot 2SbCl_3$) (Wells, Amer. Chem. Jour. XXVI, 265). Or the acid solution may be treated with a solution of lead chloride containing free chlorine. This precipitates a double chloride of cæsium and tetravalent lead ($2CsCl \cdot PbCl_4$) (Wells, Amer. Jour. Sci. [3] XLVI, 186).

(2) *From pollucite or lepidolite.* The mineral is heated with a mixture of calcium carbonate and calcium chloride, and the fused mass is cooled and extracted with water. The liquid is then evaporated to a small volume, and sulphuric acid is added to precipitate the calcium as the sulphate. After filtration, evaporation is continued until the greater part of the hydrochloric acid has been expelled. Sodium or ammonium carbonate is then added to complete the removal of the calcium salt. Upon the addition of chloroplatinic acid the cæsium and rubidium are precipitated as the salts of that acid. By the action of hydrogen upon these salts the platinum is precipitated, while the cæsium and rubidium chlorides are left in solution.

(3) *From lepidolite.* The mineral is decomposed by heating with a mixture of calcium fluoride and sulphuric acid (*vid.* Experiment 1).

The Element. *A. Preparation.* Elementary cæsium may be obtained (1) by heating cæsium hydroxide with aluminum to redness in a nickel retort (Beketoff, Bull. Acad. Petersburg IV, 247); (2) by heating cæsium hydroxide with magnesium in a current of hydrogen (Erdmann and Menke, Jour. Amer. Chem. Soc. XXI, 259, 420); (3) by heating cæsium carbonate with magnesium in a current of hydrogen (Graefe and Eckardt, Zeitsch. anorg. Chem. XXII, 158).

B. Properties. Cæsium, the most positive of the metals,

is silvery white and soft. It takes fire quickly in the air, burning to the oxide. It melts at 26° C. Like the other alkaline metals it decomposes water. Determinations of its specific gravity range from 1.88 to 2.4.

Compounds. *A. Typical forms.* The following are typical compounds of cæsium:

Oxide, Cs_2O.

Hydroxide, $CsOH$.

Carbonates, Cs_2CO_3; $CsHCO_3$.

Chloride, $CsCl$.

Double chlorides, $AgCl \cdot CsCl$; $AgCl \cdot 2CsCl$; $HgCl_2 \cdot CsCl$; $HgCl_2 \cdot 2CsCl$; $HgCl_2 \cdot 3CsCl$; $2HgCl_2 \cdot CsCl$; $5HgCl_2 \cdot CsCl$; $PbCl_4 \cdot 2CsCl$; $PbCl_2 \cdot 4CsCl$; $PbCl_2 \cdot CsCl$; $2PbCl_2 \cdot CsCl$; $2BiCl_3 \cdot 3CsCl$; $BiCl_3 \cdot 3CsCl$; $CuCl_2 \cdot 2CsCl$; $CuCl_2 \cdot 2CsCl + 2H_2O$; $2CuCl_2 \cdot 3CsCl + 2H_2O$; $CuCl_2 \cdot CsCl$; $Cu_2Cl_2 \cdot CsCl$; $Cu_2Cl_2 \cdot 3CsCl$; $Cu_2Cl_2 \cdot 6CsCl + 2H_2O$; $CdCl_2 \cdot 2CsCl$; $CdCl_2 \cdot CsCl$; $2AsCl_3 \cdot 3CsCl$; $2SbCl_3 \cdot 3CsCl$; $SnCl_2 \cdot CsCl$; $Fe_2Cl_6 \cdot 6CsCl$; $CoCl_2 \cdot 3CsCl$; $CoCl_2 \cdot 2CsCl$; $CoCl_2 \cdot CsCl + 2H_2O$; $NiCl_2 \cdot 2CsCl$; $NiCl_2 \cdot CsCl$; $MnCl_2 \cdot 2CsCl$; $2MnCl_2 \cdot 2CsCl + 5H_2O$; $MnCl_2 \cdot 2CsCl + 3H_2O$; $MnCl_2 \cdot CsCl + 2H_2O$; $MnCl_2 \cdot 2CsCl + H_2O$; $ZnCl_2 \cdot 3CsCl$; $ZnCl_2 \cdot 2CsCl$; $MgCl_2 \cdot CsCl + 6H_2O$; $AuCl_3 \cdot CsCl$; $AuCl_3 \cdot CsCl + 0.5H_2O$; $PtCl_4 \cdot 2CsCl$; $PtCl_2 \cdot 2CsCl$; $PdCl_2 \cdot 2CsCl$; $TeCl_4 \cdot 2CsCl$; $TlCl_3 \cdot 3CsCl + H_2O$; $TlCl_3 \cdot 2CsCl$; $TlCl_3 \cdot 2CsCl + H_2O$; $2TlCl_3 \cdot 3CsCl$.

Bromides, $CsBr$; $CsBr_3$; $CsBr_5$.

Double bromides, $HgBr_2 \cdot CsBr$; $HgBr_2 \cdot 2CsBr$; $HgBr_2 \cdot 3CsBr$; $2HgBr_2 \cdot CsBr$; $PbBr_2 \cdot 4CsBr$; $PbBr_2 \cdot CsBr$; $2PbBr_2 \cdot CsBr$; $CuBr_2 \cdot 2CsBr$; $CuBr_2 \cdot CsBr$; $CdBr_2 \cdot 3CsBr$; $CdBr_2 \cdot 2CsBr$; $CdBr_2 \cdot CsBr$; $2AsBr_3 \cdot 3CsBr$; $CoBr_2 \cdot 3CsBr$; $CoBr_2 \cdot 2CsBr$; $NiBr_2 \cdot CsBr$; $ZnBr_2 \cdot 3CsBr$; $ZnBr_2 \cdot 2CsBr$; $MgBr_2 \cdot CsBr + 6H_2O$; $AuBr_3 \cdot CsBr$; $TeBr_4 \cdot 2CsBr$; $2TlBr_3 \cdot 3CsBr$; $TlBr_3 \cdot CsBr$.

Iodides, CsI; CsI_3; CsI_5.

Double iodides, $HgI_2 \cdot CsI$; $HgI_2 \cdot 2CsI$; $HgI_2 \cdot 3CsI$;

$2HgI_2 \cdot CsI$; $3HgI_2 \cdot 2CsI$; $PbI_2 \cdot CsI$; $CdI_2 \cdot 3CsI$; $CdI_2 \cdot 2CsI$; $CdI_2 \cdot CsI + H_2O$; $2AsI_3 \cdot 3CsI$; $CoI_2 \cdot 2CsI$; $ZnI_2 \cdot 3CsI$; $ZnI_2 \cdot 2CsI$; $TeI_4 \cdot 2CsI$; $TlI_3 \cdot CsI$.

Mixed halides, $HgCs_3Cl_3Br_2$; $HgCs_2Cl_2Br_2$; $HgCsClBr_2$; $Hg_5CsClBr_{10}$; $HgCs_3Br_3I_2$; $HgCs_2Br_2I_2$; $HgCsBrI_2$; $HgCs_2Cl_2I_2$; $PbCs_4(ClBr)_6$; $PbCs(ClBr)_3$; $Pb_2Cs(ClBr)_5$.

Double fluorides, $2CsF \cdot ZrF_4$; $CsF \cdot ZrF_4 + H_2O$; $2CsF \cdot 3ZrF_4 + 2H_2O$.

Iodates, $CsIO_3$; $2CsIO_3 \cdot I_2O_5$; $2CsIO_3 \cdot I_2O_5 + 2HIO_3$.

Nitride, CsN_3 (Jour. Amer. Chem. Soc. xx, 225).

Nitrates, $CsNO_3$; $3CsNO_3 \cdot Cs(NO_3)_3 + H_2O$.

Sulphates, Cs_2SO_4; $CsHSO_4$; $Cs_2S_2O_7$; $Cs_2O \cdot 8SO_3$.

Alums, $CsAl(SO_4)_2 + 12H_2O$; $Cs_2SO_4 \cdot Mn_2(SO_4)_3 + 24H_2O$; $Cs_2SO_4 \cdot Ti_2O_3 \cdot 3SO_3 + 24H_2O$.

Fluosilicate, Cs_2SiF_6.

Chromates, Cs_2CrO_4; $Cs_2Cr_2O_7$.

Chloroplatinate, $CsPtCl_6$.

B. Characteristics. With few exceptions the cæsium compounds are soluble in water. They closely resemble the potassium and rubidium compounds, being for the most part isomorphous with them. A comparison of the solubilities of the alums and also of the chloroplatinates of the three elements, at a temperature of 15°–17° C., follows:

100 parts of water will dissolve

$CsAl(SO_4)_2 + 12H_2O$,	0.62 parts;	Cs_2PtCl_6,	0.18 parts.
$RbAl(SO_4)_2 + 12H_2O$,	2.30 "	Rb_2PtCl_6,	0.20 "
$KAl(SO_4)_2 + 12H_2O$,	13.50 "	K_2PtCl_6,	2.17 "

Among the important insoluble salts are the chloroplatinate (Cs_2PtCl_6), the alum ($CsAl(SO_4)_2 + 12H_2O$), and the double chlorides with tetravalent lead ($PbCl_4 \cdot 2CsCl$), tetravalent tin ($2CsCl \cdot SnCl_4$?), and trivalent antimony ($3CsCl \cdot 2SbCl_3$). The salts of cæsium color the flame violet. The spectrum shows two sharply defined lines in the blue, designated on the scale as Csα and Csβ.

Estimation, Separation, and Experimental Work. *Vid.* Rubidium.

RUBIDIUM, Rb, 85.4.

Discovery. Rubidium was discovered by Bunsen and Kirchhoff in 1861, by means of the spectroscope, in the course of some work upon a lepidolite from Saxony (J. B. (1861), 173; Chem. News III, 357). The alkaline salts had been separated by the usual methods and precipitated with platinic chloride. The precipitate, when examined with the spectroscope, showed at first only the potassium lines. When it had been boiled repeatedly with water, however, the residue gave two violet lines situated between the strontium blue line and the potassium violet line at the extreme right of the spectrum. These increased in strength as the boiling continued, and with them appeared several other lines, among which were two almost coincident with the potassium red line (α) at the extreme left. These lines, observed for the first time, marked the discovery of an element; because of their color Bunsen gave it the name Rubidium, from the Latin *rubidus*, the deepest red.

Occurrence. Rubidium, like cæsium, is widely distributed, but in very small quantities. It is found

(1) In minerals:

Lepidolite,*	$\overset{I}{R}_3Al(SiO_3)_3$,	contains	0.7–3.0%	Rb_2O.
Leucite,	$KAl(SiO_3)_2$,	"	traces	"
Spodumene,	$LiAl(SiO_3)_2$,	"	"	"
Triphylite,	$Li(Fe,Mn)PO_4$,	"	"	"
Lithiophilite,	$Li(Mn,Fe)PO_4$,	"	"	"
Carnallite,	$KMgCl_3 \cdot 6H_2O$,	"	"	"
Mica and orthoclase		contain	"	"

* The more important mineral sources are indicated by italics.

(2) In certain mineral waters, among which are the following: Ungemach, Ems, Kissingen, Nauheim, Selters, Vichy, Wildbad, Kochbrunnen (Wiesbaden), Dürkheim.

(3) In beet-root, many samples of tobacco, some coffee and tea, ash of oak and beech, crude cream of tartar, potashes, and mother-liquor from the Stassfurt potassium salt works.

Extraction. Rubidium may be extracted with cæsium from lepidolite (*vid.* Extraction of Cæsium).

The Element. *A. Preparation.* Elementary rubidium may be obtained (1) by heating the charred tartrates to a white heat (Bunsen); (2) by reducing the hydroxide or the carbonate with magnesium (Winkler, Ber. Dtsch. chem. Ges. XXIII, 51); (3) by reducing the hydroxide with aluminum (Beketoff).

B. Properties. Rubidium is a soft white metal which melts at 38° C. It takes fire in the air, burning to the oxide. It decomposes water. Its specific gravity is 1.52.

Compounds. *A. Typical forms.* The following are typical compounds of rubidium:

Oxide, Rb_2O.

Hydroxide, $RbOH$.

Carbonates, Rb_2CO_3; $RbHCO_3$.

Chloride, $RbCl$.

Double chlorides, $HgCl_2 \cdot 2RbCl$; $HgCl_2 \cdot 2RbCl + 2H_2O$; $2HgCl_2 \cdot RbCl$; $4HgCl_2 \cdot RbCl$; $PbCl_4 \cdot 2RbCl$; $2PbCl_2 \cdot RbCl$; $PbCl_2 \cdot 2RbCl + 0.5H_2O$; $BiCl_3 \cdot 6RbCl$; $BiCl_3 \cdot RbCl + 4H_2O$; $CdCl_2 \cdot 2RbCl$; $2AsCl_3 \cdot 3RbCl$; $3SbCl_3 \cdot 5RbCl$; $2SbCl_3 \cdot 3RbCl$; $SbCl_3 \cdot RbCl$; $2SbCl_3 \cdot RbCl + H_2O$; $MnCl_2 \cdot 2RbCl + 2H_2O$; $ZnCl_2 \cdot 2RbCl$; $MgCl_2 \cdot RbCl + 6H_2O$; $AuCl_3 \cdot RbCl$; $TeCl_4 \cdot 2RbCl$; $TlCl_3 \cdot 3RbCl + H_2O$; $TlCl_3 \cdot 2RbCl + H_2O$.

Chlorate, $RbClO_3$.

Perchlorate, $RbClO_4$.

Bromides, $RbBr$; $RbBr_3$.

Double bromides, $2PbBr_2 \cdot RbBr$; $PbBr_2 \cdot 2RbBr + 0.5H_2O$; $2AsBr_3 \cdot 3RbBr$; $2SbBr_3 \cdot 3RbBr$; $AuBr_3 \cdot RbBr$; $TeBr_4 \cdot 2RbBr$; $TlBr_3 \cdot 3RbBr + H_2O$; $TlBr_3 \cdot RbBr + H_2O$.
Iodides, RbI; RbI_3.
Double iodides, $AgI \cdot 2RbI$; $PbI_2 \cdot RbI + 2H_2O$; $2AsI_3 \cdot 3RbI$; $2SbI_3 \cdot 3RbI$; $TeI_4 \cdot 2RbI$; $TlI_3 \cdot RbI + 2H_2O$.
Iodates, $RbIO_3$; $RbIO_3 \cdot HIO_3$; $RbIO_3 \cdot 2HIO_3$.
Nitride, RbN_3.
Nitrates, $RbNO_3$; $3RbNO_3 \cdot Co(NO_3)_3 + H_2O$.
Cyanide, RbCN.
Sulphates, Rb_2SO_4; $RbHSO_4$; $Rb_2S_2O_7$; $Rb_2O \cdot 8SO_3$.
Alums, $RbAl(SO_4)_2 + 12H_2O$; $RbFe(SO_4)_2 + 12H_2O$; $RbCr(SO_4)_2 + 12H_2O$; $Rb_2SO_4 \cdot Ti_2O_3 \cdot 3SO_3 + 24H_2O$.
Chloroplatinate, Rb_2PtCl_6.
Silicofluoride, Rb_2SiF_6.

B. Characteristics. The rubidium compounds are very similar to those of potassium and cæsium (*vid.* Cæsium). Among the important insoluble salts are the perchlorate ($RbClO_4$), the silicofluoride (Rb_2SiF_6), the chloroplatinate (Rb_2PtCl_6), the bitartrate ($RbHO_2C_4H_4O_4$), and the alums ($RbAl(SO_4)_2 + 12H_2O$ and $RbFe(SO_4)_2 + 12H_2O$). The salts of rubidium color the flame violet. The spectrum gives two lines in the violet to the right of the cæsium lines (Rbα and Rbβ), also two lines not so distinct in the dark red (Rbγ and Rbδ), near the potassium red line, at the left of the spectrum.

Estimation of Cæsium and Rubidium. Cæsium and rubidium may be estimated in general by the methods applied to potassium. They are usually weighed as the normal sulphates, after evaporation of suitable salts with sulphuric acid and ignition of the products; other methods, however, such as the chloroplatinate and chloride methods, are possible. They may also be weighed with a fair degree of accuracy as the acid sulphates, after evaporation with an excess of sulphuric acid, and heating at 250°–270° C.

until a constant weight is obtained (Browning, Amer. Jour. Sci. [4] XII, 301).

Separation of Cæsium and Rubidium. These metals belong to the alkali group. From sodium and lithium they may be separated (1) by chloroplatinic acid, with which they form insoluble salts; and (2) by aluminum sulphate, with which they form difficultly soluble alums. From potassium they may be separated by the greater solubility of the potassium alum and chloroplatinate in water.*

Cæsium and rubidium may be separated from each other (1) by the difference in solubility of the chloroplatinates;* (2) by the difference in solubility of the alums;* (3) by the formation of the more stable and less soluble tartrate of rubidium; and (4) by the solubility of cæsium carbonate in absolute alcohol. Probably the most satisfactory methods, however, are those suggested by Wells; they depend upon the insolubility of the following salts: cæsium double chloride and iodide ($CsCl_2I$) (Amer. Jour. Sci. [3] XLIII, 17), cæsium-lead chloride (Cs_2PbCl_6) (ibid. [3] XLVI, 186), and cæsium-antimony chloride ($Cs_2Sb_2Cl_9$) (Amer. Chem. Jour. XXVI, 265).

EXPERIMENTAL WORK ON CÆSIUM AND RUBIDIUM.

Experiment 1. *Extraction of cæsium and rubidium salts from lepidolite.* Mix thoroughly in a lead or platinum dish 100 grm. of finely ground lepidolite with an equal amount of powdered fluorspar. Add 50 cm.^{3} of common sulphuric acid and stir until the mass has the consistency of a thin paste. Set aside in a draught hood until the first evolution of fumes (SiF_4 and HF) has nearly ceased. Heat on a plate or sand-bath at a temperature of 200°–300° C. until the mass is dry and hard. Pulverize

* Vid. page 4.

and extract with hot water until the washings give no precipitate on the addition of ammonium hydroxide to a few drops. Evaporate the entire solution to about 100 cm.^{3} and filter while hot to remove the calcium sulphate. Set the clear filtrate aside to crystallize. The crystals, consisting of a mixture of potassium, cæsium, and rubidium alums, with some lithium salt, should be dissolved in about 100 cm.^{3} of distilled water, and allowed to recrystallize. This process of recrystallization should be repeated until the crystals give no test before the spectroscope for either lithium or potassium. The amount of cæsium and rubidium alums obtained will of course vary with the variety of lepidolite used. An average amount of the mixed alums of potassium, cæsium, and rubidium from the first crystallization would be 10 grm. The pure cæsium and rubidium alums finally obtained should be about 3 grm. (Robinson and Hutchins, Amer. Chem. Jour. VI, 74). Lithium may be extracted from the mother-liquor (*vid.* Experiment 12).

Experiment 2. *Preparation of cæsium and rubidium sulphates* (Cs_2SO_4; Rb_2SO_4). Dissolve in water a crystal of the cæsium and rubidium alums obtained from lepidolite, add a few drops of ammonium hydroxide, and boil. Filter off the aluminum hydroxide and evaporate the filtrate to dryness. Ignite until the ammonium sulphate is removed, dissolve in a few drops of water, filter, and evaporate to dryness. Sulphates of cæsium and rubidium will remain.

Experiment 3. *Preparation of the carbonates of cæsium and rubidium* (Cs_2CO_3; Rb_2CO_3). Dissolve in water a crystal of cæsium and rubidium alums obtained from lepidolite, add an excess of barium carbonate, and boil. Filter off the alumina, barium sulphate, and excess of barium carbonate. Pass a little carbon dioxide through the clear filtrate and boil to remove traces of barium salt.

Filter. Carbonates of cæsium and rubidium will remain in solution.

Experiment 4. *Formation of the double chloride of cæsium and tetravalent lead* ($2CsCl_2 \cdot PbCl_4$). To a few cm.[3] of a one per cent. solution of a cæsium salt add a few drops of the reagent obtained by warming lead dioxide with hydrochloric acid and allowing the solution to stand until cool. Make a similar experiment, using a rubidium salt in place of the cæsium salt. Note the absence of precipitation in this case.

Experiment 5. *Precipitation of the double chloride of cæsium and antimony* ($3CsCl \cdot 2SbCl_3$). To a few cm.[3] of a one per cent. solution of a cæsium salt add some antimony trichloride in solution and evaporate to a small volume. The double chloride will be precipitated on cooling. Repeat the experiment, using a rubidium salt. Note the absence of precipitation in this case.

Experiment 6. *Precipitation of the double salt cæsium chloride and stannic chloride* ($2CsCl \cdot SnCl_4$). Make an experiment similar to Experiment 5, using stannic chloride in the place of antimonious chloride. Note the separation of the double chloride on cooling. Make a similar experiment, using a rubidium salt.

Experiment 7. *Precipitation of the chloroplatinates of cæsium and rubidium* (Cs_2PtCl_6; Rb_2PtCl_6). To a few cm.[3] of a solution of a cæsium salt add a few drops of a solution of chloroplatinic acid. Make a similar experiment with a solution of a rubidium salt.

Experiment 8. *Separation of cæsium from rubidium.* Apply the information gained in the foregoing experiments to the separation of cæsium from rubidium.

Experiment 9. *Flame tests for cæsium and rubidium.* Dip the end of a platinum wire into a solution of a cæsium salt and test the action of the flame of a Bunsen burner upon it. Repeat, using a rubidium salt.

Experiment 10. *Spectroscopic tests for cæsium and rubidium.* Test solutions of cæsium and rubidium salts before the spectroscope. Note the twin blue lines of the cæsium spectrum and the twin violet lines of the rubidium.

Experiment 11. *Negative tests of cæsium and rubidium.* Note that hydrogen sulphide, ammonium sulphide, and ammonium carbonate give no precipitates with salts of cæsium and rubidium.

LITHIUM, Li, 7.03.

Discovery. In 1817 Arfvedson, working in Berzelius's laboratory upon a petalite from Uto, Sweden, discovered an alkali which he found to differ from those already known in the following particulars: (1) in the low fusing points of the chloride and sulphate; (2) in the hydroscopic character of the chloride; and (3) in the insolubility of the carbonate. In his analysis of the mineral it had remained associated with sodium, not being precipitated by tartaric acid. To the newly discovered element the name Lithium was given, from λίθος, *stone*, because it differed from sodium and potassium in having a mineral rather than a vegetable origin (Ann. der Phys. u. Chem. (1818), XXIX, 229; Ann. Chim. Phys. [2] x, 82). It has since been found, however, not only in the mineral kingdom, but in the vegetable and animal kingdoms also.

Occurrence. Lithium is found combined as follows:

(1) In minerals:

Petalite,	$LiAl(Si_2O_5)_2$,	contains	2–5% Li_2O.
Spodumene,	$LiAl(SiO_3)_2$,	"	4–8% "
Lepidolite,	$\overset{I}{R}_3Al(SiO_3)_3$,	"	4–6% "
Zinnwaldite,	$(K,Li)_3FeAl_3Si_5O_{16}(OH,F)_2$,	"	3–4% "

Cryophyllite, complex silicates, *vid.* Zinnwaldite, contains 4–5% Li_2O.

Polylithionite, complex silicates, *vid.* Zinnwaldite, contains about 9% Li_2O.

Beryl,	$Be_3Al_2(SiO_3)_6$,	contains	0–1%	Li_2O.
Triphylite,	$Li(Fe,Mn)PO_4$,	"	8–9%	"
Lithiophilite,	$Li(Mn,Fe)PO_4$,	"	8–9%	"
Amblygonite,	$Li(AlF)PO_4$,	"	8–10%	"

Small amounts of lithium are found also in some varieties of tourmaline, in epidote, muscovite, orthoclase, and psilomelane.

(2) In certain mineral waters, among which are Dürkheim, Kissingen, Baden-Baden, Bilin, Assmannshausen, Tarasp, Kreuznach, Salzschlirf, Aachen, Selters, Wildbad, Ems, Homburg, Karlsbad, Marienbad, Egger-Franzenbad, Wheal Clifford.

(3) In seaweed, tobacco, cacao, coffee, and sugar-cane; in milk, human blood, and muscular tissue; in meteorites. It has been detected also in the atmosphere of the sun.

Extraction. Lithium may be extracted from minerals by the following methods:

(1) *From triphylite or lithiophilite.* The coarsely ground mineral is dissolved in hydrochloric acid to which nitric acid is gradually added, and the solution obtained is treated with a sufficient amount of ferric chloride to unite with all the phosphoric acid present. This solution is evaporated to dryness and the residue is extracted with hot water. The extract thus obtained is treated with barium sulphide, to remove the manganese and the last traces of iron. The barium is removed by sulphuric acid, and the filtrate is evaporated with oxalic acid and ignited. The alkalies remain as carbonates (Müller).

Lithium may be separated from the other alkalies by treating the mixed carbonates with water, lithium carbonate being comparatively insoluble.

(2) *From lepidolite (or any other silicate).* The mineral is

melted at red heat in a crucible, the melted mass is cooled rapidly in water and pulverized. Sufficient water is added to give the material the consistency of paste. Hydrochloric acid of specific gravity 1.2, equal in weight to the weight of the mineral taken, is gradually added, with stirring. The mass is allowed to stand for twenty-four hours. It is then heated again to about 100° C., with stirring, and a second portion of acid equal to the first is added. Upon several hours' heating the silica separates in the form of powder, and after treatment with nitric acid to oxidize the iron, the soluble material is separated by filtration from the silica. The filtrate is heated to the boiling-point and treated with sodium carbonate, which precipitates iron, aluminum, calcium, magnesium, manganese, etc. These are removed by filtration, and the liquid is evaporated to a small volume and filtered again if necessary. Lithium carbonate is precipitated by more sodium carbonate (Schrötter).

The Element. *A. Preparation.* Elementary lithium may be obtained by subjecting the fused chloride to electrolysis. Because of its volatility it cannot, like sodium and potassium, be prepared by heating the carbonate.

B. Properties. Lithium is a metallic element which has a silvery-white luster and which oxidizes in the air, though more slowly than potassium and sodium. It decomposes water at ordinary temperatures, and is light enough to float in petroleum. Its melting-point is 180° C.; its specific gravity is 0.59.

Compounds. *A. Typical forms.* The following are typical compounds of lithium:

Oxide, Li_2O.
Hydroxide, $LiOH$.
Carbonate, Li_2CO_3.
Chloride, $LiCl$.
Chlorate, $LiClO_3 + 0.5H_2O$.

Perchlorate, $LiClO_4 + 3H_2O$.
Bromide, LiBr.
Bromate, $LiBrO_3$.
Iodide, $LiI + 3H_2O$.
Iodate, $LiIO_3 + 0.5H_2O$.
Periodate, $LiIO_4$.
Fluorides, LiF; $LiF \cdot HF$.
Nitride, LiN_3.
Nitrite, $LiNO_2 + 0.5H_2O$.
Nitrate, $LiNO_3$.
Sulphide, Li_2S.
Sulphite, Li_2SO_3.
Sulphates, Li_2SO_4; $KLiSO_4$; $NaLiSO_4$; etc.
Phosphates, LiH_2PO_4; $Li_3PO_4 + 0.5H_2O$; $Li_4P_2O_7$.
Carbide, Li_2C_2.
Silicofluoride, $Li_2SiF_6 + 2H_2O$.

B. Characteristics. Most of the salts of lithium are easily soluble in water; the principal exceptions are the carbonate and the phosphate, which are difficultly soluble. Lithium resembles sodium more closely than it resembles the other alkalies, in that it does not form an insoluble chloroplatinate, nor a series of alums. The nitrate and the chloride are soluble in alcohol. The compounds of lithium color the flame brilliant crimson.

Estimation. Lithium is usually weighed as the sulphate or chloride.

Separation. Lithium may be separated from the other members of the alkali group (1) by the ready solubility of its chloride in amyl alcohol (Gooch, Amer. Chem. Jour. IX, 33); (2) by the solvent action of absolute ethyl alcohol upon the chloride; (3) by the insolubility of the phosphate; and (4) by the comparative insolubility of the carbonate.

EXPERIMENTAL WORK ON LITHIUM.

Experiment 12. *Extraction of lithium salts from triphylite or lithiophilite.* Dissolve 25 to 50 grm. of finely powdered mineral in common hydrochloric acid, add sufficient nitric acid to oxidize the iron, and enough ferric chloride to combine with all the phosphoric acid present. Evaporate to dryness and extract with hot water. Treat the extract with barium hydroxide in slight excess. Filter, add sulphuric acid to complete precipitation of barium sulphate, and filter again. Convert the sulphates present into carbonates by the careful addition of barium carbonate, filter, acidify the filtrate with hydrochloric acid, evaporate to dryness, and extract the lithium chloride with alcohol.

(Lithium salts may be extracted also from the mother-liquor after the extraction of cæsium and rubidium salts from lepidolite. The liquor is treated with barium carbonate in excess and is then boiled and filtered. The filtrate is acidified with hydrochloric acid, evaporated to dryness, and extracted with alcohol.)

Experiment 13. *Precipitation of lithium phosphate* (Li_3PO_4). To a solution of a lithium salt add sodium phosphate in solution.

Experiment 14. *Precipitation of lithium carbonate* (Li_2CO_3). To a few drops of a concentrated solution of a lithium salt add sodium carbonate in solution.

Experiment 15. *Solvent action of alcohol upon lithium salts.* Try the action of ethyl or amyl alcohol upon a little dry lithium nitrate or chloride.

Experiment 16. *Flame and spectroscopic tests for lithium.* (*a*) Dip a platinum wire into a solution of a lithium salt and hold in a Bunsen flame. Note the color.

(*b*) Observe the lithium flame by means of the spectroscope. Note the bright crimson line between the potassium and sodium lines.

Experiment 17. *Negative tests of lithium salts.* Note that hydrogen sulphide, ammonium hydroxide, ammonium carbonate acting upon dilute solutions, and chloroplatinic acid give no precipitate with lithium salts.

BERYLLIUM OR GLUCINUM, Be or Gl, 9.1.

Discovery. In the year 1797, Vauquelin discovered beryllium or glucinum in the mineral beryl (Ann. de Chim. XXVI, 155). After having removed the silica in the usual manner, he precipitated with carbonate of potassium, and treated the precipitate with a solution of caustic potash. The greater part of the precipitate dissolved, leaving a residue which he found to consist of a small amount of iron oxide and an oxide which dissolved in sulphuric acid. This solution gave, on evaporation, irregular crystals having a sweetish taste and forming no alum with potassium sulphate. The sweet taste suggested for the new element present the name Glucinum, from γλυκύς, *sweet.* Recently the name Beryllium, from the chief source, beryl, has come into more general use.

Occurrence. Beryllium occurs in minerals as follows:

Beryl,	$Be_3Al_2(SiO_3)_6$,	contains	11–15%	BeO.
Chrysoberyl,	$BeAl_2O_4$,	"	19–20%	"
Bertrandite,	$Be_2(Be\cdot OH)_2Si_2O_7$,	"	40–43%	"
Phenacite,	Be_2SiO_4,	"	44–46%	"
Leucophanite,	$Na(BeF)Ca(SiO_3)_2$,	"	10–12%	"
Meliphanite,	$NaCa_2Be_2FSi_3O_{10}$	"	10–14%	"
Epididymite,	$HNaBeSi_3O_8$,	"	10–11%	"
Euclase,	$Be(Al\cdot OH)SiO_4$,	"	17–18%	"
Helvite or *danalite,*	$\overset{II}{R}_5(\overset{II}{R}_2S)(SiO_4)_3$,	"	13–14%	"
Gadolinite,	$FeBe_2Y_2Si_2O_{10}$,	"	5–11%	"
Trimerite,	$Be(Mn,Ca,Fe)SiO_4$,	"	16–17%	"
Beryllionite,	$NaBePO_4$,	"	19–20%	"
Herderite,	$Ca(Be(OH,F))PO_4$,	"	15–16%	"
Hambergite,	$Be(BeOH)BO_3$,	"	53–54%	"

Extraction. Beryllium is generally extracted from beryl by one of the following methods:

(1) The mineral is fused with sodium and potassium carbonates (*vid.* Experiment 18).

(2) The finely ground mineral is fused with three times its weight of potassium fluoride. The fused mass is treated with strong sulphuric acid and warmed; by this process the silica is removed as silicon fluoride, and the alumina and potash are united to form the alum, which may be crystallized out on evaporation. The beryllium remains in solution as the sulphate, and may be removed by treatment with ammonium carbonate (*vid.* Experiments 18 and 20).

(3) The mineral is fused with calcium fluoride. This process is in general the same as the one indicated in the second method, except that calcium sulphate is formed and must be removed (Lebeau, Chem. News LXXIII, 3).

The Element. *A. Preparation.* Elementary beryllium may be obtained (1) by bringing together the vapor of the chloride and sodium in a current of hydrogen (Debray, Ann. Chim. Phys. (1855) XLIV, 5); (2) by fusing the chloride with potassium (Wöhler, Pogg. Annal. XIII, 577); (3) by heating the chloride in a closed iron crucible with sodium (Nilson and Pettersson, Ber. Dtsch. chem. Ges. XI, 381, 906); (4) by heating the oxide with magnesium (Winkler, Ber. Dtsch. chem. Ges. XXIII, 120).

B. Properties. The element beryllium is grayish to white in color. Unchanged in the air at ordinary temperatures, it burns brightly to the oxide when heated in air or in oxygen. It does not decompose hot or cold water. Heated in sulphur vapor it forms the sulphide, and in chlorine the chloride. It is soluble in dilute and in concentrated acids; also in potassium hydroxide with the liberation of hydrogen. Determinations of its specific gravity range from 1.64 to 2.1.

Compounds. *A. Typical forms.* The following are typical compounds of beryllium:

Oxide, BeO.

Hydroxide, $Be(OH)_2$.

Carbonates, $BeCO_3 + 4H_2O$; $xBeCO_3 \cdot yBeO$.

Chlorides, $BeCl_2$; $BeCl_2 + 4H_2O$; $xBeCl_2 \cdot yBe(OH)_2 + zH_2O$.

Chlorate, $Be(ClO_4)_2 + 4H_2O$.

Bromides, $BeBr_2$; $BeBr_2 + 4H_2O$.

Iodide, BeI_2.

Fluorides, BeF_2; $BeF_2 \cdot KF$; $BeF_2 \cdot 2KF$.

Nitrates, $Be(NO_3)_2 + 3H_2O$; $Be(NO_3)_2 \cdot Be(OH)_2 + 2H_2O$; $Be(NO_3)_2 \cdot 2BeO$.

Sulphates, $BeSO_4$; $BeSO_4 + 4H_2O$; $BeSO_4 + 7H_2O$.

Sulphites, $BeSO_3$; $BeSO_3 \cdot BeO$; $3BeSO_3 \cdot BeO$.

Phosphate, $Be_3(PO_4)_2 + 6H_2O$.

Ferrocyanides, $Be_2FeC_6N_6$; $Be_2Fe(CN)_6 \cdot 4Be(OH)_2$.

B. Characteristics. The compounds of beryllium closely resemble those of aluminum. The oxide is white, insoluble in water, and when freshly precipitated soluble in excess of potassium hydroxide. If this solution is diluted and boiled, the oxide is reprecipitated; in this reaction beryllium differs from aluminum. The salts of beryllium with the stronger acids (hydrochloric, nitric, and sulphuric) are soluble, like the corresponding salts of aluminum. The sulphate of beryllium does not unite with potassium sulphate to form an alum. Ammonium carbonate precipitates the basic carbonates of both aluminum and beryllium, but the beryllium carbonate is very soluble in excess and may be reprecipitated by boiling.

Estimation. Beryllium is ordinarily estimated as the oxide, (BeO), which is obtained by the ignition of the precipitated hydroxide.

Separation. Beryllium falls into the aluminum group, and it closely resembles that element in many reactions. It may be separated from aluminum (1) by boiling a dilute

solution of the two hydroxides in sodium or potassium hydroxide, beryllium hydroxide being precipitated; (2) by precipitating the basic acetate of aluminum, the beryllium salt remaining in solution; and (3) by saturating a solution of the two chlorides with hydrochloric acid gas in the presence of ether, the beryllium remaining in solution, while the aluminum chloride is precipitated (Gooch and Havens, Amer. Jour. Sci. [4] II, 416).

EXPERIMENTAL WORK ON BERYLLIUM.

Experiment 18. *Extraction of beryllium salts from beryl* ($Be_3Al_2Si_6O_{18}$). Fuse in a clay crucible 10 grm. of finely powdered mineral with 20 grm. of a mixture of sodium and potassium carbonates, and cool. Pour about 20 $cm.^3$ of common sulphuric acid over the fused mass and stir until it becomes gelatinous. Heat until the excess of sulphuric acid is driven off and extract with water. Evaporate to about 100 $cm.^3$, filter if necessary, and allow the potash alum to crystallize out. After removing the alum, saturate the filtrate with ammonium carbonate in the cold, allow it to stand for several hours, and filter. Boil the filtrate and collect the basic beryllium carbonate precipitated ($x BeCO_3 \cdot y BeO$). To purify this salt from iron, dissolve it in a small amount of acid, add potassium hydroxide in excess, filter off the ferric hydroxide precipitated, dilute the filtrate, and boil.

Experiment 19. *Precipitation of beryllium hydroxide* ($Be(OH)_2$). (*a*) To a solution of a beryllium salt add ammonium hydroxide, and note the insolubility of the precipitate in excess of that reagent.

(*b*) To another portion of the beryllium solution add a solution of potassium or sodium hydroxide, and note the solvent action of an excess.

(*c*) Dilute with water a portion of the alkaline solution

obtained in (*b*) and boil. Note the reprecipitation of the hydroxide.

(*d*) To another portion of the alkaline solution obtained in (*b*) add ammonium chloride, and boil.

(*e*) To a solution of a beryllium salt add ammonium sulphide.

Experiment 20. *Precipitation of beryllium carbonate* ($x BeCO_3 \cdot y BeO$). (*a*) To a solution of a beryllium salt add sodium or potassium carbonate in solution. Note the solvent action of an excess and the reprecipitation on boiling.

(*b*) Make a similar experiment, using ammonium carbonate.

Experiment 21. *Precipitation of beryllium phosphate* ($Be_3(PO_4)_2$). To a solution of a beryllium salt add a solution of sodium phosphate.

Experiment 22. *Precipitation of beryllium ferrocyanide* ($Be_2Fe(CN)_6 \cdot 4Be(OH)_2$). To a solution of a beryllium salt add a little potassium ferrocyanide in solution.

Experiment 23. *Negative tests of beryllium salts.* Try the action of hydrogen sulphide and ammonium oxalate upon separate portions of a solution of a beryllium salt. Add sodium acetate to a solution of a beryllium salt and boil. Note the absence of precipitation in each case.

YTTRIUM, Y, 89.

Discovery. In the year 1794 Gadolin (Kongl. Vet. Acad. Handl. xv, 137; Crell Annal. (1796) 1, 313) discovered a new earth* in a mineral from Ytterby later called Gadolinite, which had been discovered by Arrhenius and described by Geyer in 1788 (Crell Annal. (1788) 1, 229).

* The term *earth* is applied to certain metallic oxides which were formerly regarded as elementary bodies, as Y_2O_3, Er_2O_3, La_2O_3, etc., and names ending in *a* are often used in designating them, as yttria, erbia, etc. The ending *um* designates the element, as yttrium, erbium, lanthanum.

In 1797 Eckeberg confirmed Gadolin's discovery and named the new earth Yttria (Kong. Vet. Acad. Handl. XVIII, 156; Crell Annal. (1799) II, 63).

Occurrence. Yttrium occurs always in combination. Yttrium earths, chiefly Y_2O_3, are found as shown in the following table:

Gadolinite,	$FeBe_2Y_2Si_2O_{10}$	22–46%
Yttrialite,	$\overset{III}{R}_2O_3 \cdot 2SiO_2$	46–47%
Cappelenite,	complex silicates	52–53%
Melanocerite,	" "	9–10%
Caryocerite,	" "	2– 3%
Tritomite,	" "	2– 3%
Allanite or orthite,	$H\overset{II}{R}\overset{III}{R}_3Si_3O_{13}$	0– 4%
Cenosite,	$H_4Ca_2(Y,Er)_2CSi_4O_{17}$	37–38%
Thalenite,	$H_2Y_4Si_4O_{15}$	58–63%
Rowlandite,	$xY_2O_3 \cdot ySiO_2$	61–62%
Bodenite,	*vid.* Allanite	17–18%
Muromonite,	" "	37–38%
Keilhauite,	complex silicates	6– 7%
Tscheffkinite,	" "	0– 3%
Johnstrupite,	" "	1– 2%
Mosandrite,	" "	0– 3%
Rinkite,	" "	0– 1%
Xenotime,	YPO_4	54–64%
Monazite,	$(Ce,La,Di)PO_4$	0– 5%
Rhabdophanite,	$RPO_4 \cdot H_2O$	2–10%
Yttrocerite,	$2(2\overset{III}{R}F_3 \cdot 9CaF_2) \cdot 3H_2O$	14–15%
Fluocerite,	$R_2O_3 \cdot 4RF_3$	3– 4%
Samarskite,	$\overset{II}{R}_3\overset{III}{R}_2(Nb,Ta)_6O_{21}$	12–16%
Euxenite,	$\overset{III}{R}(NbO_3)_3 \cdot \overset{III}{R}_2(TiO_3)_3 \cdot \frac{3}{2}H_2O$	13–30%
Fergusonite,	$\overset{III}{R}(Nb,Ta)O_4$	30–46%
Yttrotantalite,	$\overset{II}{R}\overset{III}{R}_2(Ta,Nb)_4O_{15} \cdot 4H_2O$	17–20%

Hatchettolite, $R(Nb,Ta)_2O_6 \cdot H_2O$	0– 2%
Ånnerödite, complex niobate..................	7– 8%
Hielmite, complex stanno-tantalate............	1– 5%
Æschynite, $\overset{III}{R}_2Nb_4O_{13} \cdot \overset{III}{R}_2(Ti,Th)_5O_{13}$...........	1– 3%
Polymignite, $5RTiO_3 \cdot 5RZrO_3 \cdot R(Nb, Ta)_2O_6$......	2– 3%
Polycrase, $\overset{III}{R}(NbO_3)_3 \cdot 2\overset{III}{R}(TiO_3)_3 \cdot 3H_2O$...........	20–32%
Arrhenite, complex tantalo-niobate.............	22–23%
Rogersite, " " "	60–61%
Sipylite, complex niobate, Er_2O_3...27%; Y_2O_3...1%	

Extraction. The following are common methods for the extraction of yttrium salts from minerals:

(1) *From gadolinite* (*or any other silicate*). The finely powdered mineral is mixed with common sulphuric acid until the mass has the consistency of thick paste. It is then heated until dry and hard, pulverized, and extracted with cold water. From this extraction the oxalates are precipitated by the addition of oxalic acid; they are then washed, dried, and heated at 400° C. The oxides thus obtained are dissolved in sulphuric acid, and the solution is saturated with potassium or sodium sulphate. The double sulphates of the cerium group are precipitated, and the members of the yttrium group remain in solution.

(2) *From gadolinite.* The mineral is decomposed by aqua regia (*vid.* Experiment 24).

(3) *From samarskite.* The mineral is decomposed by hydrofluoric acid. The niobic and tantalic acids go into solution, and the yttrium earths, together with uranium oxide, remain (Lawrence Smith, Amer. Chem. Jour. v, 44).

The Element. *A. Preparation.* Elementary yttrium may be obtained (1) by heating the chloride with potassium (Berzelius); (2) by subjecting the melted double

chloride of sodium and yttrium to electrolysis (Cleve, Bull. Soc. Chim. d. Paris [2] XVIII, 193); (3) by heating the oxide with magnesium (Winkler, Ber. Dtsch. chem. Ges. XXIII, 787).

B. Properties. Yttrium is a grayish-black powder, which decomposes water only slightly at ordinary temperatures, but more rapidly on boiling, forming the oxide. Ignited on platinum in the air, it burns to the oxide with a brilliant light; in oxygen with a very intense glow. It is very soluble in dilute acids, including acetic, but is only slightly soluble in concentrated sulphuric acid. It decomposes potassium hydroxide at the boiling temperature.

Compounds. *A. Typical forms.* The following are typical compounds of yttrium:

Oxide, Y_2O_3.
Hydroxide, $Y(OH)_3$.
Carbonates, $Y_2(CO_3)_3 + 3H_2O$; $Y_2(CO_3)_3 \cdot Na_2CO_3 + 4H_2O$; $Y_2(CO_3)_3 \cdot (NH_4)_2CO_3 + 2H_2O$.
Chlorides, YCl_3; $YCl_3 + 6H_2O$; $YCl_3 \cdot 3HgCl_2 + 9H_2O$; $YCl_3 \cdot 2AuCl_3 + 16H_2O$; $2YCl_3 \cdot 3PtCl_2 + 24H_2O$.
Chlorate, $Y(ClO_3)_3 + 8H_2O$.
Perchlorate, $Y(ClO_4)_3 + 8H_2O$.
Bromides, YBr_3; $YBr_3 + 9H_2O$.
Bromate, $Y(BrO_3)_3 + 9H_2O$.
Iodide, YI_3.
Iodate, $Y(IO_3)_3 + 3H_2O$.
Periodate, $Y_2O_3 \cdot I_2O_7 + 8H_2O$.
Fluoride, $YF_3 + 0.5H_2O$.
Nitrates, $Y(NO_3)_3 + 6H_2O$; $2Y_2O_3 \cdot 3N_2O_5 + 9H_2O$.
Cyanides, $YKFe(CN)_6 + 2H_2O$; $Y(SCN)_3 + 6H_2O$.
Sulphates, $Y_2(SO_4)_3 + 8H_2O$; $Y_2(SO_4)_3 \cdot 4K_2SO_4$; $Y_2(SO_4)_3 \cdot Na_2CO_3 + 2H_2O$.
Sulphite, $Y_2(SO_3)_3 + 3H_2O$.

Seleniates, $Y_2(SeO_4)_3 + 8H_2O$; $Y_2(SeO_4)_3 \cdot K_2SeO_4 + 6H_2O$; $Y_2(SeO_4)_3 \cdot (NH_4)_2SeO_4 + 6H_2O$.
Selenites, $Y_2(SeO_3)_3 + 12H_2O$; $Y_2O_3 \cdot 4SeO_2 + 4H_2O$.
Sulphide, Y_2S_3.
Oxalate, $Y_2(C_2O_4)_3 + 9H_2O$.
Phosphates, YPO_4; $Y(PO_3)_3$; $YHP_2O_7 + 3.5H_2O$.
Chromate, $Y_2(CrO_4)_3 \cdot K_2CrO_4 + xH_2O$.
Tungstate, $Y_2(WO_4)_3 + 6H_2O$.
Carbide, YC_2.

B. Characteristics. The compounds of yttrium have few characteristic reactions. They resemble quite closely the compounds of aluminum, but yttrium differs from aluminum in having a hydroxide insoluble in excess of sodium or potassium hydroxide and in forming no alums. The salts of yttrium give no absorption spectra. Yttrium sulphate differs from the sulphate of cerium in forming no insoluble double sulphate with potassium or sodium sulphate.

Estimation. Yttrium is generally weighed as the oxide, (Y_2O_3), which has been obtained by the ignition of the hydroxide or the oxalate.

Separation. In the course of analysis the yttrium earths are precipitated with the aluminum group. They may be separated from aluminum by precipitation with oxalic acid or ammonium oxalate in faintly acid solution; in this reaction they resemble the other members of the rare-earth group (Ce, La, Di, Th, Zr, etc.). They may be separated from these by saturating a solution of the sulphates with potassium sulphate; the yttrium earths do not form a double sulphate insoluble in potassium sulphate as do the others.

For the separation of yttrium from the very rare members of its group (Yb, Er, Tr, etc.), *vid.* Dennis and Dales, Jour. Amer. Chem. Soc. XXIV, 401.

EXPERIMENTAL WORK ON YTTRIUM.

Experiment 24. *Extraction of yttrium salts from gadolinite* ($Be_2FeY_2Si_2O_{10}$). Warm 5 grm. of finely powdered mineral with aqua regia until it is completely decomposed. Evaporate on a water-bath and desiccate to remove the silica. Extract with hot water and a little hydrochloric acid, and add to the extract ammonium oxalate until precipitation ceases. Filter off the precipitate, which consists of the oxalates of the yttrium and cerium groups, together with traces of the oxalates of manganese and calcium; dry and ignite. Dissolve in a small amount of hydrochloric acid the oxides thus obtained, and saturate the solution with potassium sulphate; this precipitates the members of the cerium group as the double sulphates. Filter, and wash with a solution of potassium sulphate. From the filtrate precipitate the yttrium earths by an alkali hydroxide or oxalate. To remove the manganese and calcium, dissolve the precipitate in nitric acid, evaporate to dryness, and heat until the manganese salt is decomposed. Extract with water, filter off the oxide of manganese, treat the filtrate with ammonium hydroxide, and stir thoroughly. The calcium hydroxide will be dissolved, and the yttrium earths precipitated.

Experiment 25. *Precipitation of yttrium hydroxide* ($Y(OH)_3$). (*a*) To a solution of an yttrium salt add ammonium hydroxide.

(*b*) Repeat the experiment, using sodium or potassium hydroxide.

Note the insolubility in excess in each case.

(*c*) Precipitate yttrium hydroxide by the action of ammonium sulphide.

Experiment 26. *Precipitation of yttrium carbonate* ($Y_2(CO_3)_3$). (*a*) To a solution of an yttrium salt add ammonium carbonate.

(*b*) Repeat the experiment, using sodium or potassium carbonate.

Note the solubility in the cold upon the addition of an excess of the alkali carbonates, and the reprecipitation on boiling.

(*c*) Try the action of the common acids upon yttrium carbonate.

Experiment 27. *Precipitation of yttrium oxalate* ($Y_2(C_2O_4)_3$). To a solution of an yttrium salt add a solution of either oxalic acid or an alkali oxalate.

Experiment 28. *Precipitation of yttrium phosphates* ($Y_2(HPO_4)_3$; YPO_4). To a solution of an yttrium salt add sodium phosphate in solution (Na_2HPO_4). The precipitate is said to be of the acid form $Y_2(HPO_4)_3$. The neutral phosphate (YPO_4) is formed by treating an yttrium salt in solution with an ammoniacal phosphate.

Experiment 29. *Precipitation of yttrium ferrocyanide* ($YKFe(CN)_6$). To a solution of an yttrium salt add potassium ferrocyanide.

Experiment 30. *Precipitation of yttrium chromate* ($xY_2(CrO_4)_3 \cdot yY_2O_3$). To a solution of an yttrium salt add a solution of potassium chromate, and neutralize if necessary.

Experiment 31. *Precipitation of yttrium fluoride* (YF_3). To a solution of an yttrium salt add potassium fluoride.

Experiment 32. *Negative tests of yttrium salts.* Note that hydrogen sulphide gives no precipitate with yttrium salts, and that saturation of a solution of an yttrium salt with potassium or sodium sulphate gives no insoluble double salt.

THE GADOLINITE OR YTTRIUM EARTHS
OTHER THAN YTTRIA.

Associated with yttria, and resembling it in many reactions, are several very rare earths which, together with yttria, comprise the group called the Gadolinite or Yttrium

Earths. The metals of these very rare oxides are the following:

I.	II.
Terbium, Tb, 161–3	Samarium, Sm, 150
Erbium, Er, 166	Decipium, Dp, 171
Holmium, Ho, 162	Gadolinium, Gd, 156
Thulium, Tm, 171	
Dysprosium, Dy.	
Ytterbium, Yb, 173	
Philippium, Pp, 123–6	
Scandium, Sc, 44.1	

The elements in column II are classed by some authorities with the cerium group.

Discovery.* In 1843 Mosander (J. pr. Chem. XXX, 288) announced, as the result of his investigation of yttria, its separation into three earths, two white and one yellow. To the less basic of the white oxides he gave the name Terbium earth, to the more basic the original name Yttrium earth, and the yellow oxide he called Erbium earth.

In 1878 Marignac (Compt. rend. LXXXVII, 578) found in gadolinite the oxide of a new element which he named Ytterbium, and the same year Delafontaine (Compt. rend. LXXXVII, 559, 632) announced the isolation from a North Carolina samarskite of the earths of Decipium and Philippium.

The following year Nilson (Ber. Dtsch. chem. Ges. XII, 554), while engaged in extracting ytterbium from euxenite, separated an earth of much lower atomic weight, the unknown element of which he called Scandium. Another earth isolated in 1879 is the oxide of Samarium, discovered by Lecoq de Boisbaudran (Compt. rend. LXXXVIII, 323) in the course of an examination of the absorption spectra of the earths separated from samarskite.

In 1880 Cleve (Compt. rend. LXXXIX, 478), while work-

* For a recent and more detailed account of the discovery of these earths *vid.* Baskerville, Science, New Series, XVII, 774.

ing on erbium earth, discovered two elements, Holmium and Thulium, which he separated as the oxides.

Six years later Marignac and Lecoq de Boisbaudran (Compt. rend. CII, 902), during the study of terbium earth, separated the oxide of an unknown element named by them Gadolinium, and in the same year Lecoq de Boisbaudran (Compt. rend. CII, 1004) made the further announcement of the isolation of a new earth from the oxide of holmium, that of Dysprosium.

Occurrence. These earths are found associated with yttrium in small quantities and varying proportions (*vid.* Occurrence of Yttrium).

Extraction.* Methods for the extraction of the yttrium earths have already been given (*vid.* Extraction of Yttrium). Methods for their separation are as follows:

(1) Fractional precipitation by ammonium hydroxide (Mosander);

(2) Fractional precipitation by potassium oxalate (Delafontaine);

(3) Successive ignitions of the nitrates, and extractions with water (Bahr and Bunsen);

(4) Precipitation by means of lactic acid (Waage);

(5) Treatment with ethylsulphate (Urbain).

The Elements. The metallic elements of these earths have not been isolated.

Compounds. *A. Typical forms.* The typical compounds of five elements of the yttrium group are given on the next page.

B. Characteristics. The existence of the earths of erbium, terbium, ytterbium, scandium, and samarium has

* References: Mosander and Delafontaine, J. pr. Chem. XCIV, 297; Bahr and Bunsen, Ann. Chem. Pharm. CXXXVII, 1; Auer v. Welsbach, Monatshefte f. Chem. IV, 630; Waage, Chem. Ztg. (1895), 1072; Drossbach, Ber. Dtsch. chem. Ges. XXIX, 2452; Urbain, Chem. Ztg. (1898), 271; Dennis and Dales, Jour. Amer. Chem. Soc. XXIV, 401.

	Er 166	Tr 160	Yb 173	Sc 44	Sm 150
Oxides	Er_2O_3	Tr_2O_3	Yb_2O_3	Sc_2O_3	Sm_2O_3
	Er_2O_5				Sm_4O_9
Hydroxides	$Er_2O(OH)_4$	$Tr_2O_3+6H_2O$	$Yb_2O_3+6H_2O$	$Sc_2O_3+6H_2O$	$Sm_2O_3+6H_2O$
Chlorides	$ErCl_3$				$SmCl_3+6H_2O$
Bromides	$ErBr_3+9H_2O$				$SmBr_3+6H_2O$
Iodide	ErI_3				
Fluorides	ErF_3				$SmF_3+0.5H_2O$
Chlorate	$Er(ClO_3)_3+8H_2O$				
Perchlorate	$Er(ClO_4)_3+8H_2O$				
Bromate	$Er(BrO_3)_3+9H_2O$				
Iodates	$Er(IO_3)_3+3H_2O$				$Sm(IO_3)_3+6H_2O$
Sulphites	$Er_2(SO_3)_3+3H_2O$				$Sm_2(SO_3)_3$
Sulphates	$Er_2(SO_4)_3+8H_2O$	$Tr_2(SO_4)_3+8H_2O$	$Yb_2(SO_4)_3+8H_2O$	$Sc_2(SO_4)_3$	$Sm_2(SO_4)_3+8H_2O$
Double sulphates	$Er_2(SO_4)_3 \cdot 3K_2SO_4$			$Sc_2(SO_4)_3+3K_2SO_4$	$2Sm_2(SO_4)_3+9K_2SO_4$
	$Er_2(SO_4)_3 \cdot 5Na_2SO_4$				$Sm_2(SO_4)_3 \cdot Na_2SO_4$
	$Er_2(SO_4)_3 \cdot (NH_4)_2SO_4$				$Sm_2(SO_4)_3 \cdot (NH_4)_2SO_4$
Dithionate	$Er_2(S_2O_6)_3+18H_2O$				
Selenites	$Er_2(SeO_3)_3+5H_2O$		$Yb_2(SeO_3)_3$	$Sc_2(SeO_3)_3+H_2O$	
Seleniates	$Er_2(SeO_4)_3+5H_2O$				$Sm_2(SeO_4)_3+8H_2O$
Nitrates	$Er(NO_3)_3+6H_2O$	$Tr(NO_3)_3+6H_2O$			$Sm(NO_3)_3+6H_2O$
Phosphates	$ErPO_4+H_2O$				$SmPO_4$
Pyrophosphates	$Er_2H_2(P_2O_7)_2+7H_2O$				$Sm_2(HP_2O_7)_2+7H_2O$
Carbonates	$Er_2O_3 \cdot 2CO_2+2H_2O$	$Tr_2(CO_3)_3+xH_2O$			$Sm_2(CO_3)_2+3H_2O$
Oxalates	$Er_2(C_2O_4)_3+12H_2O$		$Yb_2(C_2O_4)_3+10H_2O$	$Sc_2(C_2O_4)_3+6H_2O$	$Sm_2(C_2O_4)_3+10H_2O$
Acetates	$Er(C_2H_3O_2)_3+2H_2O$	$Tr(C_2H_3O_2)_3$	$Yb(C_2H_3O_2)_3+2H_2O$		$Sm(C_2H_3O_2)_3+4H_2O$
Sulphide	Er_2S_3				

been quite definitely established. The other members of the gadolinite group are still more or less in doubt. Of the five mentioned above, the first four closely resemble yttrium. Solutions of terbium, ytterbium, and scandium salts give no absorption spectra. The salts of erbium are of a rosy tint, and give an absorption spectrum. The double sulphates of these four elements respectively with potassium sulphate are soluble in a solution of potassium sulphate, the ytterbium and scandium salts being more soluble, however, than those of erbium and terbium. Samarium resembles cerium. Its salts are yellowish, and the solutions give an absorption spectrum. The double sulphate with potassium sulphate is insoluble in a solution of potassium sulphate.

CERIUM, Ce, 140.

Discovery. In the course of the analysis of a mineral from Riddarhyttan, Sweden, in 1803, Klaproth discovered an earth which, while resembling yttria in many of its reactions, differed from it in being insoluble in carbonate of ammonium, and in acquiring, when ignited, a light brown color. Because of this latter peculiarity, the name Ochroite suggested itself to him, from ὠχρός, *yellow brown* (Phil. Mag. XIX, 95). At the same time, and independently of Klaproth, Berzelius and Hisinger made the same discovery. Their name for the new element was Cerium, chosen in honor of the discovery of the planet Ceres by Piazzi in 1801 (Phil. Mag. XX, 155; XXII, 193).

Occurrence. Cerium is found in many minerals, associated, usually, with lanthanum and didymium.

	Contains	
	Ce_2O_3	$Di_2O_3+La_2O_3$
Cerite, $(Ca,Fe)(CeO)(Ce_2 \cdot 3OH)(SiO_3)_3$	24–65%	7–35%
Allanite or orthite, $H\overset{II}{R}\overset{III}{R}_3Si_3O_{13}$	1–18%	1–16%
Gadolinite, $Be_2FeY_2Si_2O_{10}$	1–10%	2–20%

	Contains Ce_2O_3	$Di_2O_3+La_2O_3$
Cappelenite, complex silicates.......	1– 2%	2– 3%
Melanocerite, " "	20–21%	20–21%
Caryocerite, " "	14–15%	20–21%
Tritomite, " "	19–21%	21–26%
Tscheffkinite, " silico-titanates..	12–20%	17–20%
Johnstrupite, " " "	12–13%	*
Mosandrite, " " "	16–26%	*
Rinkite, " " "	21–22%	*
Mackintoshite, $UO_2\cdot 3ThO_2\cdot 3SiO_2\cdot 3H_2O$....	45–46%†	
Monazite, (Ce, La, Di)PO_4..........	16–36%	20–24%
Churchite, $\overset{II}{R}_3P_2O_8\cdot 4H_2O$............	50–51%	
Xenotime, YPO_4..................	0–11%	*
Rhabdophanite, $RPO_4\cdot H_2O$.........	23%	55%
Fluocerite, $R_2O_3\cdot 4RF_3$.............	39–46%	30–36%
Tysonite, (Ce, La, Di)F_3.............	40%	30%
Yttrocerite, $(2\overset{III}{R}F_3\cdot 9CaF_2)\cdot 3H_2O$.....	5%	5%
Parisite, $(CaF)(CeF)Ce(CO_3)_3$.......	38%	15%
Bastnaesite, (Ce, La, Di)$_2C_3O_9\cdot$(Ce, La, Di)F_3..	28–41%	35–46%
Lanthanite, $La_2(CO_3)_3\cdot 9H_2O$........		52%
Samarskite, $\overset{II}{R}_3\overset{III}{R}_2(Nb,Ta)_6O_{21}$........	2– 5%	*
Fergusonite, $\overset{III}{R}(Nb,Ta)O_4$............	0– 9%	*
Euxenite, $\overset{III}{R}(NbO_3)_3\cdot\overset{III}{R}_2(TiO_3)_3\cdot\frac{3}{2}H_2O$.	2– 8%	
Zirkelite, $(Ca,Fe)O\cdot 2(Zr, Ti, Th)O_2$...	2– 3%	
Polycrase, $\overset{III}{R}(NbO_3)_3\cdot 2\overset{III}{R}(TiO_3)_3\cdot 3H_2O$	2– 3%	
Polymignite, $5RTiO_3\cdot 5RZrO_3\cdot R(Nb,Ta)_2O_6$....	6%	5%
Æschynite, $\overset{III}{R}_2Nb_4O_{13}\cdot\overset{III}{R}_2(Ti,Th)_6O_{13}$..	18%	5%

* Included under Ce_2O_3. † $Ce_2O_3+ThO_2$.

	Contains Ce_2O_3	$Di_2O_3+La_2O_3$
Hielmite, formula doubtful..........	0.5- 1%	
Ånnerödite, " "	2- 3%	
Yttrotantalite, $\overset{II}{R}\overset{III}{R}_2(Ta,Nb)_4O_{15}\cdot 4H_2O$.	0- 2%	
Sipylite, complex niobate...........	1%	8%
Pyrochlore, $RNb_2O_6\cdot R(Ti,Th)O_3$.....	5- 7%	
Arrhenite, formula doubtful.........	2- 3%	*

Extraction. Cerium is generally extracted from cerite through decomposition of the mineral by heating it with strong sulphuric acid (*vid.* Experiment 33). The decomposition may be accomplished also by the action of a mixture of strong hydrochloric and nitric acids, but better results may be expected by the former method.

The Element. *A. Preparation.* Elementary cerium may be obtained (1) by reducing the chloride with sodium or potassium (Mosander); (2) by subjecting the double chloride of cerium and sodium to electrolysis (Pogg. Annal. CLV, 633).

B. Properties. In appearance cerium resembles iron. While fairly stable in dry air, it oxidizes quickly in moist air. It takes fire more easily than magnesium, and melts at a lower temperature than silver and at a higher temperature than antimony. It is soluble in dilute acids, but is not attacked by concentrated sulphuric or nitric acid. It combines with chlorine, bromine, and iodine, forming salts. Its specific gravity is 6.6.

Compounds. *A. Typical forms.* The following are typical forms of the two classes of cerium compounds:

Oxides..........	Ce_2O_3	CeO_2
Hydroxides.....	$Ce_2O_3\cdot 6H_2O$	$2CeO_2\cdot 3H_2O$
Carbonates......	$Ce_2(CO_3)_3+5H_2O$	$Ce(CO_3)_2+0.5H_2O$
Chloride........	$CeCl_3$	
Bromide.	$CeBr_3$	
Iodide..........	CeI_3	
Perchlorate......	$Ce(ClO_4)_3+8H_2O$	

* Included under Ce_2O_3.

Bromate........	$Ce(BrO_3)_3 + 9H_2O$	
Iodate..........	$Ce(IO_3)_3 + 2H_2O$	
Fluorides.......	CeF_3	$CeF_4 + H_2O$
Cyanide.........	$Ce(CN)_3$	
Ferrocyanides...	$Ce_4(FeC_6N_6)_3 + 30H_2O$	
	$CeKFeC_6N_6 + 3H_2O$	
Ferricyanide.....	$CeFeC_6N_6 + 8H_2O$	
Sulphocyanide ..	$Ce(CSN)_3 + 7H_2O$	
Sulphide........	Ce_2S_3	
Sulphite........	$Ce_2(SO_3)_3 + 3H_2O$	
Sulphates.......	$Ce_2(SO_4)_3 +$ 3, 5, 6, 8, 9, and $12H_2O$	$Ce(SO_4)_2 + 4H_2O$
Double sulphates.	$Ce_2(SO_4)_3 \cdot 3K_2SO_4 + 2H_2O$	$Ce(SO_4)_2 \cdot 2K_2SO_4 + 2H_2O$
	$Ce_2(SO_4)_3 \cdot 3Na_2SO_4 + 2H_2O$	
	$Ce_2(SO_4)_3 \cdot (NH_4)_2SO_4 + 8H_2O$	
Nitrates........	$Ce(NO_3)_3 + 6H_2O$	$Ce(NO_3)_4$
Double nitrates. .	$Ce_2(NO_3)_6 \cdot 3Zn(NO_3)_2 + 24H_2O$	$2Ce(NO_3)_4 \cdot 4KNO_3 + 3H_2O$
	$Ce_2(NO_3)_6 \cdot 3Co(NO_3)_2 + 24H_2O$, etc.	$2Ce(NO_3)_4 \cdot 4(NH_4)NO_3 + 3H_2O$
Phosphates......	$CePO_4$	$(CeO_2)_4 \cdot (P_2O_5)_6 + 26H_2O$
Oxalate.........	$Ce_2(C_2O_4)_3$	
Carbide.........		CeC_2

B. Characteristics. Cerium exists in compounds in two conditions of oxidation. The higher or ceric salts are easily reduced to the lower or cerous condition by the ordinary reducing agents (e.g. H_2S, SO_2, $H_2C_2O_4$, etc.), and the cerous salts may be oxidized to the ceric condition by oxidizing agents (e.g. $PbO_2 + HNO_3$, H_2O_2, $KMnO_4$, etc.). In general the cerous salts are colorless, and the ceric yellow. The lower oxide of cerium, (Ce_2O_3), on ignition goes over to the higher condition, (CeO_2). The cerous salts are the more stable, and consequently they form the greater number. They resemble the yttrium salts in many of their reactions, and are distinguishable from them chiefly by the formation of the double sulphates with sodium sulphate and potassium sulphate respectively, by the comparative insolubility of the carbonate in ammonium carbonate, and by the possibility of oxidation to a higher condition. Solutions of pure cerium salts give no absorption spectra.

Estimation. *A. Gravimetric.* Cerium is usually determined gravimetrically as the dioxide, (CeO_2), obtained by the ignition of the hydroxide or the oxalate.

B. Volumetric. (1) When ceric oxide, (CeO_2), is treated with hydrochloric acid in the presence of potassium iodide, iodine is set free, according to the following equation:

$$2CeO_2 + 8HCl + 2KI = 2CeCl_3 + 4H_2O + 2KCl + I_2.$$

The iodine may be estimated in acid solution by standard thiosulphate, or in alkaline solution by standard arsenious acid (Bunsen, Ann. Chem. Pharm. CV, 49; Browning, Amer. Jour. Sci. [4] VIII, 451).

(2) When cerium oxalate is dissolved in sulphuric acid the oxalic acid may be readily determined by potassium permanganate, and the amount of cerium present may be thus estimated (Stolba, Zeitsch. anal. Chem. XIX, 194; Browning, Amer. Jour. Sci. [4] VIII, 457).

(3) When yellow ceric compounds are treated with hydrogen dioxide in acid solution, they are reduced to cerous compounds, with bleaching of color (Knorre, Zeitsch. angew. Chem. (1897), 685):

$$2Ce(SO_4)_2 + H_2O_2 = Ce_2(SO_4)_3 + H_2SO_4 + O_2.$$

Separation. Cerium falls into the analytical group with aluminum, iron, etc. Together with the other rare earths it may be separated from these by oxalic acid or oxalate of ammonium. For separation from the yttrium earths, *vid.* page 24.

Cerium may be separated from lanthanum and didymium * by the following methods: (1) by treating the hydroxides suspended in a solution of caustic potash with

* For an instructive review of the methods for the separation of cerium, lanthanum, and didymium, see P. Mengel, Zeitsch. anorg. Chem. XIX (1899), 67.

chlorine gas, as in Experiment 33 (Mosander, J. pr. Chem. XXX, 267); (2) by treating a neutral solution of the cerium earths with an excess of a hypochlorite and boiling, thus precipitating ceric oxide (Popp, Ann. Chem. Pharm. CXXXI, 359); (3) by treating a solution of the cerium earths with sodium peroxide, in place of the hypochlorite in (2) (O. N. Witt, Chem. Ind. (1896), 11, 19); (4) by treating the oxalates of the cerium earths with warm dilute nitric acid; thus separating the cerium as basic nitrate (Auer von Welsbach, Monatshefte f. Chem. V, 508); (5) by treating a solution of the salts with hydrogen dioxide in the presence of magnesium acetate (Meyer and Koss, Ber. Dtsch. chem. Ges. XXXV, 672).

From thorium cerium may be separated (1) by repeated precipitations on boiling with sodium thiosulphate (Fresenius and Hintz, Zeitsch. anal. Chem. XXXV, 543); (2) by boiling with potassium nitride (Dennis and Kortright, Amer. Chem. Jour. XVI, 79):

$$Th(NO_3)_4 + 4KN_3 + 4H_2O = Th(OH)_4 + 4KNO_3 + 4HN_3;$$

(3) by boiling a nearly neutral solution of the chlorides with copper and cuprous oxide (Lecoq de Boisbaudran, Compt. rend. XCIX, 525); (4) by the action of fumaric acid in 40% alcohol upon solutions of the salts in 40% alcohol (Metzger, Jour. Amer. Chem. Soc. XXIV, 901). In all of these methods the thorium is precipitated.

Cerium is separated from zirconium by fusion of the oxides with acid potassium fluoride, and extraction with water and a little hydrofluoric acid; the potassium fluozirconate is dissolved, and the thorium and cerium remain * (Delafontaine, Chem. News LXXV, 230).

Experimental Work. *Vid.* Lanthanum and Didymium.

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* For the action of organic bases as precipitants of the rare earths, *vid.* Jefferson, Jour. Amer. Chem. Soc. XXIV, 540; Baskerville, Science, New Series, XVI, 215; Kolb, J. pr. Chem. [2] LXVI, 59; Allen, Jour. Amer. Chem. Soc. XXV, 421.

LANTHANUM, La, 138.77; DIDYMIUM, Di, 142.3.

(PRASEODYMIUM, Pr, 140.5; NEODYMIUM, Nd, 143.6.)

Discovery. In 1839 Mosander found that when the nitrate of cerium had been ignited, he was able to extract from it by very dilute acid an earth which differed in properties from that of cerium, while from the portion remaining undissolved he obtained the reactions of the cerium earth. He supposed the unknown substance of the newly discovered earth to be an element, and named it Lanthanum, from λανθάνειν, *to hide* (Pogg. Annal. XLVI, 648; Liebig, Annal. XXXII, 235).

In 1841, while engaged in further work upon the extraction of mixtures of cerium and lanthanum oxides by dilute nitric acid, he succeeded in separating from the lanthanum oxide another earth, rosy in color, going over to dark brown on being heated. Reserving for the residual oxide the original name Lanthanum earth, he called the base of the new oxide Didymium, from δίδυμος, *twin*,—a name suggested by its close relationship to lanthanum and its almost invariable occurrence with it (Pogg. Annal. LVI, 503).

In 1885 Auer von Welsbach announced that by long-continued fractional crystallization of the double nitrates of ammonium with lanthanum and didymium in the presence of strong nitric acid, he had separated didymium into two elements (Sitzungsber. d. k. Acad. d. Wiss. (1885) XCII, Heft I, II, 317; Ber. Dtsch. chem. Ges. XVIII, 605). The lanthanum crystallized out first, and afterward the decomposition of the didymium took place. To these new elements he gave the names Praseodymium (πράσινος, *leek-green*) and Neodymium (νέος, *new*).

In 1888 Krüss and Nilson stated, as the result of their work on the absorption spectrum of didymium, that they

had discovered indications of the presence of no less than eight elements (Ber. Dtsch. chem. Ges. xx, 2134, 3067). These results, however, have not as yet been fully confirmed. At the present time the existence of praseodymium and neodymium is generally accepted.

(Though the term "didymium" does not designate an element, it is still in general use, and for the sake of convenience it is employed in the following pages. While there is a considerable body of information concerning didymium, its constituent elements have not yet been so fully studied,—perhaps because of the long and tedious operation involved in their separation. For that reason, at all events, no experimental work on them is given in this book.)

Occurrence. Lanthanum and didymium are found almost invariably associated with cerium (*vid.* Occurrence of Cerium).

Extraction. In the process of extracting cerium from cerite (*vid.* Experiment 33), the oxalates of cerium, lanthanum, and didymium are precipitated together. Lanthanum and didymium must next be separated from cerium, and then from each other. Afterward didymium may be decomposed into its two constituents. Several methods of accomplishing these three steps are indicated under Separation of Cerium, and of Lanthanum and Didymium.

The Elements. I. LANTHANUM. *A. Preparation.* The element lanthanum may be obtained (1) by reducing the chloride with potassium; (2) by subjecting the double chloride of lanthanum and sodium to electrolysis.

B. Properties. Lanthanum is a metallic element of a lead-gray color. It decomposes cold water slowly and hot water more rapidly, with the evolution of hydrogen. It oxidizes easily in the air. Its specific gravity is from 6.04 to 6.19.

II. Didymium. Elementary praseo- and neodymium have not been isolated.

A. Preparation. Didymium may be prepared from the salts by the methods indicated for lanthanum (*vid.* Preparation of Lanthanum).

B. Properties. Metallic didymium is yellowish white. It decomposes cold water slowly and oxidizes in the air. Its specific gravity is 6.54.

Compounds. *A. Typical forms.* The following are typical compounds of lanthanum and didymium:

Oxides	La_2O_3	Di_2O_3
		Di_2O_5
Hydroxides	$La(OH)_3$	$Di(OH)_3$
Chlorides	$LaCl_3+7H_2O$	$DiCl_3+6H_2O$
Oxychlorides	$La(OCl_3)$	$Di(OCl)_3$
Chlorate	$La(ClO_3)_3$	
Perchlorates	$La(ClO_4)_3+9H_2O$	$Di(ClO_4)_3+9H_2O$
Bromides	$LaBr_3+7H_2O$	$DiBr_3+6H_2O$
Bromates	$La(BrO_3)_3+9H_2O$	$Di(BrO_3)_3+9H_2O$
Iodates	$La_2(IO_3)_6+3H_2O$	$Di(IO_3)_3+6H_2O$
Periodates	$La(IO_4)_3+2H_2O$	$Di(IO_4)_3+4H_2O$
		$DiO(IO_4)+4H_2O$
Sulphites	$La_2(SO_3)_3+4H_2O$	$Di_2(SO_3)_3+6H_2O$
Sulphates	$La_2(SO_4)_3+9H_2O$	$Di_2(SO_4)_3+8H_2O$
Double sulphates	$La_2(SO_4)_3\cdot 3K_2SO_4$	$Di_2(SO_4)_3\cdot 3K_2SO_4$
	$La_2(SO_4)_3\cdot Na_2SO_4+2H_2O$	$Di_2(SO_4)_3\cdot Na_2SO_4+2H_2O$
	$La_2(SO_4)_3\cdot (NH_4)_2SO_4+8H_2O$	$Di_2(SO_4)_3\cdot (NH_4)_2SO_4+8H_2O$
Dithionates	$La_2(S_2O_6)_3+16H_2O$	$Di_2(S_2O_6)_3+24H_2O$
Selenites	$La_2(SeO_3)_3+9H_2O$	$Di_2(SeO_3)_3+6H_2O$
Seleniates	$La_2(SeO_4)_3+6H_2O$	$Di_2(SeO_4)_3+8H_2O$
Double seleniates	$La_2(SeO_4)_3\cdot K_2SeO_4+9H_2O$	$Di_2(SeO_4)_3\cdot K_2SeO_4$
	$La_2(SeO_4)_3\cdot Na_2SeO_4+4H_2O$	$Di_2(SeO_4)_3\cdot Na_2SeO_4$
	$La_2(SeO_4)_3\cdot (NH_4)_2SeO_4+9H_2O$	$Di_2(SeO_4)_3\cdot (NH_4)_2SeO_4$
Nitrates	$La(NO_3)_3+6H_2O$	$Di(NO_3)_3+6H_2O$
Phosphates	$LaPO_4$; also meta and pyro forms	$DiPO_4+H_2O$; also meta and pyro forms
Arseniates	$La_2H_3(AsO_4)_3$	$Di_2H_3(AsO_4)_3$
Arsenites	$La_2H_3(AsO_3)_3$	$Di_2H_3(AsO_3)_3$
Carbonates	$La_2(CO_3)_3+3H_2O$	$Di_2(CO_3)_3+6H_2O$; also double salts with K, Na, and NH_4 carbonates

Oxalates........	$La_2(C_2O_4)_3$	$Di_2(C_2O_4)_3+12H_2O$
Chromates......	$La_2(CrO_4)_3$	$Di_2(CrO_4)_3+7H_2O$
Molybdates......	$LaH_3(MoO_4)_3$	$DiH_3(MoO_4)_3$
Tungstates......	$La_2(WO_4)_3$	$Di(WO_4)_3$
Sulphides.......	La_2S_3	Di_2S_3

The following compounds of praseo- and neodymium have been described:

Oxides..........	Pr_2O_3	Nd_2O_3
	Pr_4O_7	
	Pr_2O_4	Nd_2O_4?
	Pr_2O_5?	Nd_2O_5?
Carbonate.......	$Pr_2(CO_3)_3+8H_2O$	
Chlorides........	$PrCl_3+7H_2O$	$NdCl_3+6H_2O$
Bromide.	$PrBr_3+6H_2O$	
Sulphates.	$Pr_2(SO_4)_3+8H_2O$	$Nd_2(SO_4)_3+8H_2O$
	$Pr_2O_2SO_4$	$Nd_2O_2SO_4$
	$PrH_3(SO_4)_3$	$NdH_3(SO_4)_3$
Double sulphates.	$Pr_2(SO_4)_3 \cdot 3K_2SO_4+H_2O$	
	$Pr_2(SO_4)_3 \cdot (NH_4)_2SO_4+8H_2O$	
Sulphides.......	Pr_2S_3	Nd_2S_3
Selenite.........	$Pr_2(SeO_3)_3 \cdot H_2SeO_3+3H_2O$	
Seleniate........	$Pr_2(SeO_4)_3+8H_2O$	
Double seleniate.	$Pr_2(SeO_4)_3 \cdot K_2SeO_4+4H_2O$	
Nitrates........	$Pr(NO_3)_3+6H_2O$	$Nd(NO_3)_3$
Double nitrates. .	$Pr(NO_3)_3 \cdot 2(NH_4)NO_3+4H_2O$	
	$Pr(NO_3)_3 \cdot 2NaNO_3+H_2O$	
Double cyanide. .	$2Pr(CN)_3 \cdot Pt(CN)_2+18H_2O$	
Oxalate.........	$Pr_2(C_2O_4)_3+10H_2O$	

B. Characteristics. The compounds of lanthanum, didymium, and cerium in the cerous condition are very similar in their behavior toward chemical reagents. The compounds of lanthanum and didymium may be distinguished from those of cerium by the absence of yellow color on the addition of oxidizing agents,—a color characteristic of the higher oxide of cerium. Lanthanum may be distinguished from didymium by the colorlessness of its salts and by the absence of an absorption spectrum. Didymium salts in general are of a rosy color and give a distinctive absorption spectrum.

The compounds of praseo- and neodymium have not been sufficiently studied to allow any detailed description of their characteristics to be given. Neodymium salts are rose-colored and are very similar in appearance and in behavior to the salts of the original didymium. The oxide Nd_2O_3 is bluish. Praseodymium salts are green. While their chemical form resembles closely the form of the neodymium salts, higher oxides are definitely known in the case of praseodymium. The ordinary oxide Pr_2O_3 is greenish white; the higher oxide Pr_4O_7 is nearly black. Each of the two elements has distinctive spectra, spark and absorption. Mixed, the elements give the didymium spectrum.

Estimation. Like cerium, lanthanum and didymium are generally estimated as oxides, obtained by ignition of the hydroxides or oxalates.

Separation. *A. Lanthanum from didymium.* Lanthanum may be separated from didymium (1) by dissolving the sulphates in water at 9° C. and gradually raising the temperature,—the lanthanum sulphate separating first (Hermann, J. pr. Chem. LXXXII, 385); (2) by heating the nitrates at 400°–500° C. and extracting with water,—the didymium tending to form an insoluble basic nitrate (Damour and Deville, Bull. Soc. Chim. d. Paris II, 339); (3) by dissolving half of a given amount of the oxides in warm dilute nitric acid, then adding the other half, with constant stirring, cooling the mass, and extracting with water (*vid.* Experiment 33). The didymium will be found in the residue (Auer von Welsbach, Monatshefte f. Chem. V, 508).

B. Praseodymium from neodymium. Didymium may be separated into its two constituents (1) by making several hundred fractional crystallizations, first of the double nitrate of ammonium and didymium and later of the double nitrate of sodium and didymium, in the presence of

nitric acid,—the neodymium salt being the more soluble (Auer von Welsbach, Sitzungsber. d. k. Acad. d. Wiss. (1885) XCII, Heft I, II, 317; (2) by allowing nitric acid to act upon the oxalates,—the praseodymium salt being the more soluble (Scheele, Ber. Dtsch. chem. Ges. XXXII, 417); (3) by treating the sulphates with water,—the praseodymium sulphate being the more soluble (Muthmann and Rölig, Ber. Dtsch. chem. Ges. XXXI, 1718); (4) by making fractional precipitations of a solution of didymium nitrate by means of sodium acetate and hydrogen peroxide,—the praseodymium separating first (Meyer and Koss, Ber. Dtsch. chem. Ges. XXXV, 676); (5) by saturating a cold concentrated solution of citric acid with the hydroxides free from ammonia and excess of water, then filtering and heating,—the green citrate of praseodymium being precipitated, insoluble in hot water (Baskerville, Science, New Series, XVI, 214).

EXPERIMENTAL WORK ON CERIUM, LANTHANUM, AND DIDYMIUM.

Experiment 33. *Extraction of cerium, lanthanum, and didymium salts from cerite* $(Ca,Fe)(CeO)(Ce_2 \cdot 3OH)(SiO_3)_3$. Treat 25 grm. of finely powdered cerite with common sulphuric acid and stir until the mass has the consistency of thick paste. Heat until the excess of sulphuric acid is removed and then keep the mass for some time at low redness. Cool, pulverize, and digest with cold water until no further precipitate appears upon the addition of ammonium oxalate to a few drops of the extract. Pass hydrogen sulphide into the solution to remove traces of bismuth and copper. Filter, and to the filtrate add oxalic acid to complete precipitation of the oxalates of cerium, lanthanum, and didymium. Ignite the oxalates, and dissolve in hydrochloric acid the oxides obtained. To this solution add potassium hydroxide

until the precipitation of the hydroxides is complete. Make up the volume of the liquid in which the hydroxides are suspended to about 200 cm.[3] Add about ·5 grm. of potassium hydroxide to insure an excess, and pass a slow current of chlorine gas through, stirring from time to time, until the liquid is no longer alkaline in reaction and the precipitate has assumed a deep-yellow color. By this process the cerium hydroxide is oxidized to the dioxide, which remains undissolved, and the lanthanum and didymium hydroxides are dissolved. When the separation is complete, a portion of the washed precipitate dissolved in hydrochloric acid should give no evidence of the presence of didymium,—for example, no absorption spectrum (*vid.* Experiment 43). The absence of didymium at this point is considered sufficient evidence of the absence of lanthanum. To the solution containing the lanthanum and didymium, the cerium dioxide having been removed by filtration, add oxalic acid until the precipitation is complete. Filter off the oxalates, wash, dry, and ignite. Dissolve one half of the oxides obtained by this process in the least possible amount of warm, dilute nitric acid, and add the remainder of the oxides to the solution. Stir thoroughly, and when the mass is cool extract with water. The didymium tends to be in the residue and the lanthanum in solution.

Experiment 34. *Reduction and oxidation of cerium compounds.* (*a*) To a small portion of the carefully washed cerium dioxide obtained in the previous experiment add a little hydrochloric acid diluted with an equal volume of water and boil. Note the evolution of chlorine and the ultimate colorless solution of cerium chloride, ($CeCl_3$).

(*b*) To a portion of the solution obtained in (*a*) add a few drops of ammonium hydroxide in excess and some hydrogen dioxide. Note the orange-yellow precipitate (CeO_3?). Other oxidizing agents, such as sodium hypo chlorite, sodium peroxide, lead dioxide, potassium per-

manganate, etc., may be used. Boil the solution holding the precipitate in suspension and note that the deep-yellow color changes to a lighter yellow. The precipitate becomes essentially the dioxide, (CeO_2).

(*c*) To another portion of the washed cerium dioxide from Experiment 33 ($2CeO_2 \cdot 3H_2O$) add hydrochloric acid as before, and also a crystal of potassium iodide in the cold. Note the liberation of iodine according to the reaction $2CeO_2 + 8HCl + 2KI = 2CeCl_3 + 2KCl + I_2 + 4H_2O$.

Experiment 35. *Precipitation of cerous hydroxide,* ($Ce(OH)_3$). (*a*) To a solution of cerium chloride add sodium, potassium, or ammonium hydroxide in solution. Note the insolubility of the hydroxide in excess of these reagents.

(*b*) Repeat the experiment with tartaric acid present in the solution.

Experiment 36. *Precipitation of cerous carbonate,* ($Ce_2(CO_3)_3$). (*a*) To a solution of cerium chloride add a solution of sodium or potassium carbonate. Note the comparative insolubility in excess.

(*b*) Repeat the experiment, using ammonium carbonate as the precipitant.

(*c*) Try the action of the common acids upon the carbonate of cerium.

Experiment 37. *Precipitation of cerium oxalate,* ($Ce_2(C_2O_4)_3$). (*a*) To a solution of a cerium salt add oxalic acid or an oxalate. Note the crystalline character of the precipitate, especially after the liquid has been stirred and boiled.

(*b*) Try the action of hydrochloric acid upon cerium oxalate.

Experiment 38. *Precipitation of the double sulphate of cerium and potassium or sodium,* ($Ce_2(SO_4)_3 \cdot 3K_2SO_4$ or $Ce_2(SO_4)_3 \cdot Na_2SO_4$). To a few drops of a concentrated solution of a cerous salt add a small portion of a saturated solution of sodium or potassium sulphate.

Experiment 39. *Precipitation of cerium phosphate,* ($CePO_4$). (*a*) To a solution of a cerous salt add sodium phosphate in solution.

(*b*) Try the action of hydrochloric and acetic acids upon separate portions of the precipitate.

Experiment 40. *Precipitation of cerous fluoride,* (CeF_3). To a solution of cerium chloride add potassium fluoride in solution.

Experiment 41. *Precipitation of the ferrocyanide of cerium,* ($Ce_4(FeC_6N_6)_3$). (*a*) To a solution of cerium chloride add potassium ferrocyanide.

(*b*) Note that potassium ferricyanide gives no precipitate.

Experiment 42. *Comparison of lanthanum and didymium with cerium.* (*a*) Perform Experiments 35 to 41 inclusive upon dilute solutions of lanthanum and didymium salts.

(*b*) Note that pure lanthanum and didymium salts give no change of color with oxidizing agents. Compare with cerium salts (*vid.* Experiment 34).

Experiment 43. *Didymium absorption spectrum.* Place a solution of a didymium salt between the slit of the spectroscope and a luminous flame. Note the dark bands. Observe that cerium and lanthanum salts in solution show no absorption bands when free from didymium.

Experiment 44. *Negative test of the salts of cerium, lanthanum, and didymium.* Note that hydrogen sulphide gives no precipitate with salts of this group. Ammonium sulphide precipitates the hydroxides, not the sulphides.

THORIUM, Th, 232.5.

Discovery. As early as the year 1818 Berzelius, after working on a mineral from Fahlun, Sweden, believed that he had discovered a new earth (Annal. der Phys. u. Chem.

(1818) XXIX, 247). He gave it the name Thoria, from Thor, son of the Scandinavian war god Odin. Some years later however, he identified the supposed new earth as chiefly a basic phosphate of yttrium (Pogg. Annal. IV, 145). In 1828 Esmark discovered, near Brevig, Norway, the mineral since known as thorite. From it Berzelius isolated an unknown earth; its similarity to the substance described by him some ten years earlier prompted the name Thoria (Pogg. Annal. XVI, 385).

Occurrence. Thorium is found in combination in certain rare minerals:

	Contains ThO_2
Thorite or *orangite*, $ThSiO_4$	48–72%
Yttrialite, $R_2O_3 \cdot 2SiO_2$	12%
Zircon, $ZrSiO_4$	0– 2%
Orthite or allanite, $H\overset{II}{R}\overset{III}{R}_3Si_3O_{13}$	0– 3%
Mackintoshite, $UO_2 \cdot 3ThO_2 \cdot 3SiO_2 \cdot 3H_2O$	45–46%*
Thorogummite, $UO_3 \cdot 3ThO_2 \cdot 3SiO_2 \cdot 6H_2O$	41–42%
Caryocerite, complex silicates	13–14%
Tritomite, " "	8– 9%
Zirkelite, $(Ca,Fe)O \cdot 2(Zr,Ti,Th)O_2$	7– 8%
Monazite, $(Ce,La,Di)PO_4$	0–18%
Xenotime, YPO_4	0– 3%
Æschynite, $\overset{III}{R}_2Nb_4O_{13} \cdot \overset{III}{R}_2(Ti,Th)_5O_{13}$	15–17%
Euxenite, $\overset{III}{R}(NbO_3)_3 \cdot \overset{III}{R}_2(TiO_3)_3 \cdot \frac{3}{2}H_2O$	0– 6%
Tscheffkinite, complex silico-titanates	0–21%
Pyrochlore, $RNb_2O_6 \cdot R(Ti,Th)O_3$	0– 8%
Samarskite, $\overset{II}{R}_3\overset{III}{R}_2(Nb,Ta)_6O_{21}$	0– 3%
Ånnerödite, formula doubtful	2– 3%
Polymignite, $5RTiO_3 \cdot 5RZrO_3 \cdot R(Nb,Ta)_2O_6$	3– 4%

* $ThO_2 + Ce_2O_3$.

Extraction. Two common methods for the extraction of thorium salts are here indicated:

(1) *From thorite.* The mineral is decomposed by heating it with sulphuric acid (*vid.* Experiment 33). After the extraction of the sulphate with cold water, the solution is heated to 100° C. and an impure sulphate of thorium comes down. By repeated solution of the precipitate in cold water and reprecipitation by means of heat a pure sulphate is finally obtained (Delafontaine, Ann. Chem. Pharm. CXXXI, 100).

(2) *From monazite.* The mineral is decomposed by sulphuric acid and the oxalates are precipitated by oxalic acid (*vid.* Experiment 45).

The Element. *A. Preparation.* Elementary thorium may be obtained (1) by heating the double chloride of thorium and potassium with metallic sodium (Nilson); (2) by reducing the double fluoride of potassium and thorium with potassium.

B. Properties. Thorium is known in two forms, (1) that of a grayish, glistening powder, and (2) crystalline. It is stable in the air, and does not decompose water, even at 100° C. When heated in a current of chlorine, bromine, or iodine it glows and forms the salt. It is soluble in dilute hydrochloric and sulphuric acids, in concentrated sulphuric acid with the liberation of sulphur dioxide, and in aqua regia. It is acted upon very slowly by nitric acid, and is not attacked by the alkali hydroxides. The specific gravity of thorium in the amorphous condition is 10.97; in crystalline form 11.2.

Compounds. *A. Typical forms.* The following are typical compounds of thorium:

Oxides, ThO_2; Th_2O_7.
Hydroxide, $Th(OH)_4$.
Chlorides, $ThCl_4$; also double salts with KCl and NH_4Cl.

Bromide, $ThBr_4$.
Iodide, ThI_4.
Fluoride, $ThF_4 + 4H_2O$.
Chlorate, $Th(ClO_3)_4$.
Perchlorate, $Th(ClO_4)_4$.
Bromate, $Th(BrO_3)_4$.
Iodate, $Th(IO_3)_4$.
Sulphite, $Th(SO_3)_2 + H_2O$.
Sulphates, $Th(SO_4)_2 + 9H_2O$; also double salts with K_2SO_4; Na_2SO_4; and $(NH_4)_2SO_4$.
Selenite, $Th(SeO_3)_2 + H_2O$.
Seleniate, $Th(SeO_4)_2 + 9H_2O$.
Nitrate, $Th(NO_3)_4 + 12H_2O$.
Phosphate, $Th_3(PO_4)_4 + 4H_2O$.
Pyrophosphate, $ThP_2O_7 + 2H_2O$.
Ferrocyanide, $ThFe(CN)_6 + 4H_2O$.
Silicate, $ThSiO_4$.
Carbonates, $Th(CO_3)_2$; $Th(CO_3)_2 \cdot 3Na_2CO_3 + 12H_2O$.
Oxalate, $Th(C_2O_4)_2 + 2H_2O$.
Sulphide, ThS_2.

B. Characteristics. The compounds of thorium resemble in chemical form those of cerium in the ceric condition. Thorium resembles cerium also in having a hydroxide insoluble in the alkali hydroxides, and in forming a double sulphate with potassium sulphate, insoluble in excess of that precipitant. The salts of thorium are colorless except where the element is combined with an acid having a color of its own. Possibly the most distinctive reactions of thorium compounds are the ready formation of a soluble double oxalate when ammonium oxalate is added in excess to a thorium salt in solution, and the precipitation of the hydroxide when a solution of a thorium salt is boiled with potassium hydronitride (Dennis and Kortright, Amer. Chem. Jour. XVI, 79).

Estimation. Thorium is ordinarily estimated as the

oxide (ThO_2), obtained by ignition of the hydroxide, the nitrate, or the oxalate.

Separation. Thorium is a member of the aluminum group. Together with the rare earths cerium, yttrium, zirconium, etc., it may be separated from other members of the group by oxalic acid. Methods for its separation from yttrium and cerium have already been given (*vid.* pages 24 and 35).

From zirconium thorium may be separated (1) by the action of acids upon the potassium double sulphates,—the zirconium salt being the more soluble; (2) by the action of an excess of oxalic acid upon the oxalates,—the zirconium oxalate dissolving first; (3) by fusion with acid potassium fluoride; (4) by the action of dimethylamine upon solutions of the salts,—thorium hydroxide being precipitated (Kolb, J. pr. Chem. [2] LXVI, 59).

EXPERIMENTAL WORK ON THORIUM.

Experiment 45. *Extraction of thorium oxide from monazite.* Treat 25 grm. of finely ground monazite with common sulphuric acid according to the method already described (*vid.* Experiment 33). Precipitate the oxalates with oxalic acid,—not ammonium oxalate,—boil, and collect on a filter. Treat the precipitate with a large excess of ammonium oxalate and boil. Cool, filter, and to the filtrate add hydrochloric acid. Collect and ignite the oxalate of thorium thus precipitated.

Note. This method may be employed for the extraction of thorium from discarded Welsbach-light mantles.

Experiment 46. *Precipitation of thorium hydroxide,* ($Th(OH)_4$). (*a*) To a solution of a thorium salt add sodium, potassium, or ammonium hydroxide. Note the insolubility of the hydroxide in excess of the precipitant.

(*b*) To a solution of a thorium salt add sodium thiosulphate in solution and boil.

Experiment 47. *Precipitation of thorium carbonate*, ($Th(CO_3)_2$). (*a*) To a solution of a thorium salt add potassium or sodium carbonate. Note the solubility of the precipitate in excess and the reprecipitation on boiling.

(*b*) Repeat, using ammonium carbonate.

(*c*) Note the solvent action of the common acids upon thorium carbonate.

Experiment 48. *Precipitation of the oxalate of thorium*, ($Th(C_2O_4)_2 + 2H_2O$). (*a*) To a solution of a thorium salt add a solution of oxalic acid. Note the insolubility in excess of the precipitant.

(*b*) Repeat, using ammonium oxalate as the precipitant. Note the solubility in excess, especially on warming, and the reprecipitation upon the addition of hydrochloric acid.

(*c*) Try the solvent action of ammonium acetate upon thorium oxalate.

Experiment 49. *Precipitation of the double sulphate of potassium and thorium*, ($Th(SO_4)_2 \cdot 2K_2SO_4 + 2H_2O$ or $Th(SO_4)_2 \cdot 4K_2SO_4 + 2H_2O$). Saturate a solution of a thorium salt with potassium sulphate. (The corresponding sodium salt ($Th(SO_4)_2 \cdot Na_2SO_4 + 6H_2O$) is somewhat soluble in excess of sodium sulphate.)

Experiment 50. *Precipitation of thorium phosphate*, ($Th_3(PO_4)_4 + 4H_2O$). To a solution of a thorium salt add sodium phosphate in solution. Orthophosphoric acid is said to precipitate an acid phosphate ($ThH_2(PO_4)_2$).

Experiment 51. *Precipitation of thorium fluoride*, ($ThF_4 + 4H_2O$). To a solution of a thorium salt add a solution of potassium fluoride. Double salts with thorium fluoride may also form ($xKF \cdot yThF_4$ typical).

Experiment 52. *Precipitation of thorium ferrocyanide*, ($ThFe(CN)_6 + 4H_2O$). To a solution of a thorium salt add a solution of potassium ferrocyanide. Note the absence of precipitation with potassium ferricyanide.

Experiment 53. *Action of hydrogen peroxide upon*

salts of thorium. To a solution of a thorium salt add a little hydrogen peroxide, and warm.

Experiment 54. *Negative test of thorium salts.* To a solution of a thorium salt add hydrogen sulphide. Note that ammonium sulphide precipitates the hydroxide, not the sulphide.

ZIRCONIUM, Zr, 90.7.

Discovery. While engaged in the analysis of the zircons, in 1788, Klaproth found one variety containing 31.5% of silica, 0.5% of the oxides of iron and nickel, and 68% of an earth which differed from all earths previously known to him. He observed that it was soluble in the acids, but insoluble in the alkalies, in the latter respect differing from alumina (Ann. de Chim. 1, 238). The fact that zircon was the source of the new earth suggested the name Zirconium for the element.

Occurrence. Zirconium is found combined, widely diffused, but always in small quantities.

	Contains ZrO_2
Zircon, $ZrSiO_4$	61–67%
Rosenbuschite, $6CaSiO_3 \cdot 2Na_2ZrO_2F_2 \cdot (TiSiO_3 \cdot TiO_3)$	18–20%
Låvenite, $R(Si,Zr)O_3 \cdot Zr(SiO_3)_2 \cdot RTa_2O_6$	28–32%
Wöhlerite, $12R(Si,Zr)O_3 \cdot RNb_2O_6$	15–23%
Hainite, allied to låvenite, etc.	undetermined
Hiortdahlite, $4Ca(Si,Zr)O_3 \cdot Na_2ZrO_2F_2$	21–22%
Eudialyte, $Na_{13}(Ca,Fe)_6Cl(Si,Zr)_{20}O_{52}$	11–17%
Catapleiite, $H_4(Na_2,Ca)ZrSi_3O_{11}$	29–40%
Elpidite, $H_6Na_2ZrSi_6O_{18}$	20–21%
Eucolite, *vid.* Eudialyte	12–16%
Auerbachite, *vid.* Zircon	38–69%
Cyrtolite, " "	41–42%
Alvite, " "	48–51%
Tritomite, complex silicates	1– 2%
Erdmannite, " "	0– 5%

	Contains ZrO_2
Polymignite, $5RTiO_3 \cdot 5RZrO_3 \cdot R(Nb,Ta)_2O_6$	29–30%
Arrhenite, complex	3– 4%
Sipylite, "	2– 3%
Zirkelite, $(Ca,Fe)O \cdot 2(Zr,Ti,Th)O_2$	52–53%
Baddeleyite, ZrO_2	96.5%

Extraction. Zirconium salts may be extracted from zircon by the following methods:

(1) The finely powdered mineral is fused with acid potassium fluoride (*vid.* Experiment 55) (Marignac, Ann. Chim. Phys. [3] LX, 257).

(2) The mineral is fused with potassium bisulphate and the fused mass extracted with dilute boiling sulphuric acid. The basic sulphate ($3ZrO \cdot SO_3$) is left as a residue (Franz, Ber. Dtsch. chem. Ges. II, 58).

(3) The finely powdered mineral is heated with a mixture of sodium hydroxide and sodium fluoride, the mass is cooled, pulverized, and extracted with water. The residue, which consists mainly of sodium zirconate, is digested with hydrochloric acid until dissolved. After the solution has been evaporated to a small volume the zirconium oxychloride separates in crystalline form (Bailey, Proc. Royal Soc. XLVI, 74).

The Element. *A. Preparation.* Elementary zirconium may be obtained in the amorphous condition (1) by reducing potassium fluozirconate with potassium (Berzelius), and (2) by reducing the oxide with magnesium (Phipson). It may be obtained in crystalline form by heating potassium fluozirconate with aluminum (Troost), and in graphitic form by heating sodium fluozirconate with iron at 850° C.

B. Properties. (1) Zirconium in the amorphous condition is a black powder. Heated in the air it burns brightly to the oxide. It oxidizes also when fused with alkali nitrates, carbonates, and chlorates, and is only slightly attacked by acids.

(2) In crystalline form zirconium has much the appearance of antimony. Heated in the air it oxidizes very slowly. It is not acted upon by fusion with alkali nitrates, carbonates, or chlorates, but is soluble in the acids upon the application of heat. Its specific gravity is 4.15.

Compounds. *A. Typical forms.* The following are typical compounds of zirconium:

Oxides, ZrO_2; ZrO_3.
Hydroxide, $Zr(OH)_4$.
Chlorides, $ZrCl_4$; also double salts with KCl and NaCl.
Oxyhalides, $ZrOCl_2+3H_2O$; $ZrOBr_2+3H_2O$; $ZrI(OH)_3+3H_2O$.
Bromide, $ZrBr_4$.
Iodide, ZrI_4.
Fluoride, ZrF_4.
Sulphite, $Zr(SO_3)_2$.
Sulphates, $Zr(SO_4)_2+4H_2O$; $3ZrO_2 \cdot SO_3$.
Selenite, $Zr(SeO_3)_2$.
Nitrate, $Zr(NO_3)_4+5H_2O$.
Phosphate, $Zr_3(PO_4)_4$.
Pyrophosphate, ZrP_2O_7.
Carbonate, $3ZrO_2 \cdot CO_2+8H_2O$.
Oxalates, $Zr(C_2O_4)_2 \cdot 2Zr(OH)_4$; $Zr(C_2O_4)_2 \cdot K_2C_2O_4 \cdot H_2C_2O_4+8H_2O$.
Zirconates, Na_4ZrO_4; Li_2ZrO_3, etc.
Fluozirconate, K_2ZrF_6.

B. Characteristics. In chemical structure the compounds of zirconium bear a strong resemblance to those of thorium, titanium, germanium, and silicon. The oxide, in its behavior as a base toward oxides having more acidic qualities, resembles the oxide of thorium (ThO_2). With the weaker acids, carbonic and oxalic, it shows weaker basic properties in the formation of basic salts. With strong bases it manifests acidic properties, like the oxide of titanium, and forms zirconates (*vid.* Typical Forms,

above). The hydroxide of zirconium is insoluble in excess of the alkali hydroxides, the double sulphate with potassium is insoluble in a solution of potassium sulphate, and the oxalate is soluble in ammonium oxalate. Solutions of pure zirconium salts are said to give no precipitate with hydrofluoric acid or potassium hydronitride. Turmeric paper, when dipped into a solution of a zirconium salt and dried, is colored orange.

Estimation. Zirconium is usually weighed as the oxide (ZrO_2) obtained by ignition of the hydroxide or oxalate.

Separation. Zirconium is a member of the aluminum group, and with the rare earths may be roughly separated from other members of the group by the action of oxalic acid (*vid.* page 24). For the separation from yttrium, cerium, and thorium see under those elements. The separation of zirconium from iron and titanium has received a good deal of attention from chemists. Some of the methods that have been suggested follow.

From iron zirconium may be separated (1) by the action of water upon an ethereal solution of the chlorides,—the oxychloride of zirconium being precipitated (Matthews, Jour. Amer. Chem. Soc. xx, 846); (2) by the action of gaseous hydrochloric acid and chlorine at a temperature of about 200° C. upon the mixed oxides,—the ferric chloride being volatilized (Havens and Way, Amer. Jour. Sci. [4] VIII, 217); (3) by treatment with phenylhydrazine,—the zirconium being precipitated (Allen, Jour. Amer. Chem. Soc. xxv, 426); (4) by the action of sulphurous acid on neutral solutions,—the zirconium being precipitated (Baskerville, Jour. Amer. Chem. Soc. xvi, 475).

From titanium zirconium may be separated (1) by boiling a solution containing the two elements with dilute sulphuric and acetic acids,—titanic acid being precipitated free from zirconium (Streit and Franz, J. pr. Chem. CVIII, 75; Zeitsch. anal. Chem. IX, 388); (2) by treating solu-

tions acid with sulphuric or hydrochloric acid with zinc until the titanium is reduced to the condition of the sesquioxide, and then adding potassium sulphate,—the zirconium-potassium sulphate being precipitated (Pisani, Compt. rend. LVII, 298; Chem. News X, 91, 218); (3) by adding ammonium hydroxide to a boiling hydrofluoric acid solution of the salts,—the titanic acid being precipitated (Demarçay, Compt. rend. C, 740; J. B. (1885), 1929).

EXPERIMENTAL WORK ON ZIRCONIUM.

Experiment 55. *Extraction of zirconium salts from zircon.* Fuse 5 grm. of finely powdered zircon in a platinum or nickel crucible with about 15 grm. of acid potassium fluoride. Pulverize the fused mass and extract with hot water containing a few drops of hydrofluoric acid.* Filter immediately through a rubber funnel into a rubber beaker. As the filtrate cools, potassium fluozirconate crystallizes out. It may be purified by recrystallization.

Experiment 56. *Precipitation of zirconium hydroxide,* ($Zr(OH)_4$). (*a*) To a solution of a zirconium salt add potassium, sodium, or ammonium hydroxide. Note the insolubility in excess. (*b*) To a solution containing zirconium add sodium thiosulphate in solution and boil.

Experiment 57. *Precipitation of zirconium carbonate,* ($3ZrO_2 \cdot CO_2 + 8H_2O$). (*a*) To a solution of a zirconium salt add sodium or potassium carbonate. Note the partial solubility in excess.

(*b*) Use ammonium carbonate as the precipitant. Note the solvent action of an excess and the precipitation of the hydroxide on boiling.

(*c*) Try the action of the common acids upon separate portions of zirconium carbonate.

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* Glass or porcelain dishes must not be used when hydrofluoric acid is present.

Experiment 58. *Precipitation of zirconium oxalate*, ($Zr(C_2O_4)_2 \cdot 2Zr(OH)_4$). (*a*) To a solution of a zirconium salt add a solution of oxalic acid. Note the effect of an excess in the cold and on warming.

(*b*) Use ammonium oxalate as the precipitant. Note the solvent action of an excess and the reprecipitation by ammonium hydroxide.

Experiment 59. *Precipitation of zirconium phosphate*, ($xZrO_2 \cdot yP_2O_5$, *basic*). To a solution of a zirconium salt add sodium phosphate. Orthophosphoric acid precipitates the normal phosphate ($Zr_3(PO_4)_4$).

Experiment 60. *Precipitation of zirconium ferrocyanide*, ($ZrFeC_6N_6$?). To a solution of a zirconium salt add potassium ferrocyanide.

Experiment 61. *Action of zirconium salts upon turmeric paper*. Dip a piece of turmeric paper into a solution of a zirconium salt acidified with hydrochloric acid. Dry on the side of a test-tube or beaker, as in testing for boric acid. Note the yellowish-red color.

Experiment 62. *Negative tests of zirconium salts*. Note that neither hydrogen sulphide nor potassium fluoride gives a precipitate with zirconium salts. Ammonium sulphide precipitates the hydroxide, not the sulphide.

GERMANIUM, Ge, 72.

Discovery. In 1886 Clemens Winkler announced the presence of a new element in the silver mineral argyrodite, which had been discovered the previous year by Weisbach, in the Himmelsfürst mine near Freiberg (Ber. Dtsch. chem. Ges. XIX, 210). According to Winkler's analysis of argyrodite, the sum of its component parts was seven per cent. less than it should have been; and although he repeated the analysis several times with great care, the outcome was always the same. This uniformity of result forced

upon him the conclusion that an unknown element was probably present; and after much careful and patient work he was successful in isolating it and investigating its properties. On heating the mineral out of contact with the air, he obtained a dark-brown fusible sublimate, which proved to be chiefly two sulphides, that of the new element, named by him Germanium, and the sulphide of mercury.

Occurrence. Germanium is found in combination in a few rare minerals.

	Contains Ge
Argyrodite, $4Ag_2S \cdot GeS_2$	6–7%
Canfieldite, $4Ag_2S \cdot (Ge,Sn)S_2$	1.82%
Euxenite, $\overset{III}{R}(NbO_3)_3 \cdot \overset{III}{R}_2(TiO_3)_3 \cdot \frac{3}{2}H_2O$	traces

Extraction. Germanium salts have been extracted from argyrodite by the following methods:

(1) A Hessian crucible is heated to redness, and small quantities of a mixture consisting of three parts of sodium carbonate, six parts of potassium nitrate, and five parts of the mineral are gradually put in. After being heated for some time the molten mass is poured into an iron dish and allowed to cool. The salt mass may then be removed from the silver, pulverized, and extracted with water. The extract is treated with sulphuric acid and evaporated until all the nitric acid is driven off. The residue is dissolved in water and allowed to stand until the oxide of germanium separates from the solution.

(2) The mineral is heated to redness in a current of hydrogen, and the sublimate, consisting of a mixture of germanium and mercuric sulphides, is collected. This sublimate is treated with ammonium sulphide, which dissolves the sulphide of germanium, forming a sulpho salt. After filtration, the solution is acidified with hydrochloric acid, which precipitates the germanium as the sulphide.

The Element. *A. Preparation.* Elementary germanium may be obtained (1) by heating the oxide with carbon; (2) by heating the oxide in a current of hydrogen.

B. Properties. Germanium is a grayish-white, metallic element, having a fine luster, and crystallizing in regular octahedra. It volatilizes slightly when heated in hydrogen or nitrogen at about 1350° C.; its melting-point is about 900° C. In the air it does not oxidize at ordinary temperatures, but when heated goes over to the oxide GeO_2. It is not attacked by dilute hydrochloric acid, is oxidized by nitric acid, and is dissolved by aqua regia. It is dissolved also by sulphuric acid, with the evolution of sulphur dioxide. It combines directly with chlorine, bromine, and iodine. Its specific gravity is 5.46.

Compounds. *A. Typical forms.* The following are typical compounds of germanium:

Oxides	GeO	GeO_2
Hydroxides	$Ge(OH)_2$	$Ge(OH)_4$?
Chlorides	$GeCl_2$	$GeCl_4$
Oxychloride		$GeOCl_2$
Bromide		$GeBr_4$
Iodide		GeI_4
Fluorides	GeF_2?	GeF_4?; K_2GeF_6; H_2GeF_6
Sulphides	GeS	GeS_2
Chloroform		$GeHCl_3$
Ethyl		$Ge(C_2H_5)_4$

B. Characteristics. The germanium compounds are known in two conditions of oxidation; those of the higher form are the more stable and comprise the larger group. Germanium resembles carbon and silicon in the formation of a chloroform, and tin in the formation of two sulphides which dissolve in ammonium sulphide, giving sulpho salts. The sulphide GeS_2 is a white powder slightly soluble in water. The lower sulphide, GeS, when precipitated, is of a

reddish-brown color; when obtained by the reduction of the higher sulphide it is a grayish-black crystalline substance of metallic luster. This sulphide, also, is slightly soluble in water. The dioxide is a white powder soluble in alkalies, but almost completely insoluble in acids. The tetrachloride is a liquid which fumes in damp air and is decomposed by water.

Estimation. Germanium is usually precipitated as the sulphide, converted by nitric acid into the oxide (GeO_2), and weighed as such.

Separation. Germanium may be separated from most of the elements by the formation of a soluble sulpho salt with ammonium sulphide; when the solution is acidified the sulphide is precipitated. Germanium may be separated from arsenic, antimony, and tin as follows: the solution of the sulpho salts is exactly neutralized with sulphuric acid, allowed to stand twelve hours, and filtered; the filtrate is evaporated to a small volume, treated with ammonia and sulphate of ammonium, acidified with sulphuric acid, and saturated with hydrogen sulphide. Germanium sulphide is precipitated (Truchot, Les Terres Rares, 294).

TITANIUM, Ti, 48.1.

Discovery. In the year 1791 McGregor (Crell Annal. (1791) I, 40, 103) discovered a new "metal" in a magnetic sand found in Menachan, Cornwall. This sand he named Menachinite, and the newly discovered element Menachite. Four years later Klaproth announced the discovery of a new earth in a rutile which he was engaged in studying (Klapr. Beitr. I, 233). To the metal of this earth he gave the name Titanium, in allusion to the Titans. In 1797, however, he found that titanium was identical with menachite (Klapr. Beitr. II, 236).

Occurrence. Titanium is found combined in many

minerals, but never in considerable quantity in any one locality.

	Contains TiO_2
Rutile, TiO_2.	90–100%
Dicksbergite, *vid.* Rutile.	90–100%
Brookite, TiO_2.	90–100%
Octahedrite, TiO_2.	90–100%
Pseudobrookite, $Fe_4(TiO_4)_3$.	44– 53%
Perofskite, $CaTiO_3$.	58– 59%
Ilmenite, $FeTiO_3$.	3– 59%
Geikielite, $MgO \cdot TiO_2$.	67– 68%
Senaite, $(Fe,Pb)O \cdot 2(Ti,Mn)O_2$.	57– 58%
Zirkelite, $(Ca,Fe)O \cdot 2(Zr,Ti,Th)O_2$.	14– 15%
Knopite, $RO \cdot TiO_2$	54– 59%
Derbylite, $6FeO \cdot 5TiO_2 \cdot Sb_2O_5$.	34– 35%
Lewisite, $5CaO \cdot 2TiO_2 \cdot 3Sb_2O_5$.	11– 12%
Mauzeliite, $4(Ca,Pb)O \cdot TiO_2 \cdot 2Sb_2O_5$.	7– 8%
Titanite, $CaTiSiO_5$.	34– 42%
Neptunite, $\overset{I}{R}_2\overset{II}{R}TiSi_4O_{12}$.	17– 18%
Hainite, formula doubtful.	undetermined
Lamprophyllite, formula doubtful.	"
Keilhauite, complex silicate.	26– 36%
Schlormenite, $3CaO(Fe,Ti)_2O_3 \cdot 3(Si,Ti)O_2$.	12– 22%
Guarinite, $CaTiSiO_5$	33– 34%
Tscheffkinite, complex silicates.	16– 21%
Astrophyllite, $(Na,K)_4(Fe,Mn)_4Ti(SiO_4)_4$.	7– 14%
Johnstrupite, complex silicates.	7– 8%
Mosandrite, " "	5– 10%
Rinkite, " "	13– 14%
Dysanalyte, $6(Ca,Fe)TiO_3 \cdot (Ca,Fe)Nb_2O_6$.	40– 59%
Pyrochlore, $RNb_2O_6 \cdot R(Ti,Th)O_3$,	5– 14%
Æschynite, $\overset{III}{R}_2Nb_4O_{13} \cdot \overset{III}{R}_2(Ti,Th)_5O_{13}$.	21– 22%
Polymignite, $5RTiO_3 \cdot 5RZrO_3 \cdot R(Nb,Ta)_2O_6$.	18– 19%

	Contains TiO_2
Euxenite, $\overset{III}{R}(NbO_3)_3 \cdot \overset{III}{R}_2(TiO_3)_3 \cdot \frac{3}{2}H_2O$	20– 23%
Polycrase, $\overset{III}{R}(NbO_3)_3 \cdot 2\overset{III}{R}(TiO_3)_3 \cdot 3H_2O$.	25– 29%

Titanium has been found also in sand on the banks of the North Sea, in some mineral waters, in certain varieties of coal, in meteorites, and by means of the spectroscope it has been detected in the atmosphere of the sun. It has been found in the ash of oak, apple, and pear wood, in cow peas, in cotton-seed meal, and in the bones of men and animals. *Vid.* also Baskerville, Jour. Amer. Chem. Soc. XXI, 1099.

Extraction. Titanium salts may be extracted from rutile by the following methods:

(1) The mineral is fused with three parts of a mixture of sodium and potassium carbonates and the fused mass is extracted with water. The titanium, as a sodium or potassium titanate, remains, together with some tin and iron, in the insoluble residue. This mass is treated with strong hydrochloric acid until dissolved. The solution is then diluted, and the tin is removed by hydrogen sulphide. The sulphide of tin is filtered off, the filtrate is made ammoniacal with ammonium hydroxide and again treated with hydrogen sulphide. The iron is precipitated as the sulphide, and the titanium as the hydroxide. After filtration the precipitate is suspended in water and a current of sulphur dioxide is passed through until the black sulphide of iron has dissolved, leaving the oxide of titanium.

(2) The mineral is fused with three parts of acid potassium fluoride and the fused mass is extracted with hot water and a little hydrofluoric acid. The titanium separates, on cooling, as the potassium fluotitanate ($K_2TiF_6 + H_2O$).

(3) The mineral is fused with six parts of acid potassium sulphate (*vid.* Experiment 63).

The Element. *A. Preparation.* Elementary titanium

may be obtained (1) by heating potassium fluotitanate with potassium (Berzelius and Wöhler); (2) by passing the vapor of the chloride ($TiCl_4$) through a bulb tube containing sodium.

B. Properties. As prepared in the laboratory, titanium is a dark-gray powder. It does not decompose water at ordinary temperatures and acts on heated water but slightly. When heated in the air it combines with the oxygen, burning brightly to the oxide (TiO_2); in oxygen the combination is accompanied with brilliant light. Titanium is readily soluble in warm hydrochloric acid, and is attacked by dilute hydrofluoric, nitric, sulphuric, and acetic acids. It combines with chlorine. It combines also with nitrogen, forming nitrides.

Compounds. *A. Typical forms.* The following are typical compounds of titanium:

Oxides...	TiO; (Ti_3O_4); Ti_2O_3; (Ti_7O_{12});	TiO_2; (Ti_2O_5);	TiO_3
Hydroxides		$Ti(OH)_4$	$Ti(OH)_6$
Chlorides ..	Ti_2Cl_6	$TiCl_4$	
Bromide...		$TiBr_4$	
Iodide.....		TiI_4	
Fluoride ...		TiF_4	
Titanofluorides.....		$\overset{I}{R}_2TiF_6$, etc.	
Sulphides ..	Ti_2S_3	TiS_2	
Nitrides....		Ti_3N_4; Ti_5N_6; TiN_2	
Carbide			TiC
Titanates...		$\overset{II}{R}TiO_3$; $\overset{I}{R}_2TiO_3$	
Acids (*vid.* Hydroxides)...		H_2TiO_3	

B. Characteristics. Although a number of oxides of titanium are known, the dioxide is the form generally found, and the salts of that type are by far the most numerous and important. The oxide (TiO_2) resembles the oxide of zirconium (ZrO_2) in acting as a weak base. It forms

salts with the strong acids, but does not combine with the weak acids. It unites with the strong bases to form titanates, ($\overset{II}{R}TiO_3$ and $\overset{I}{R}_2TiO_3$). It has less basic and more acidic properties than the oxide of zirconium. The tetrachloride is a colorless liquid which fumes in the air. Titanium, in its behavior toward reagents, resembles quite closely both niobium and tantalum, with which it is often found associated (*vid.* Occurrence).

Estimation. *A. Gravimetric.* Titanium is usually precipitated as the acid, either by ammonium hydroxide or by boiling a dilute solution acidified with acetic or sulphuric acid; the precipitate is ignited and the element is determined as the oxide (TiO_2).

B. Volumetric. Titanium is estimated volumetrically (1) by treating with hydrogen dioxide a definite amount of the titanium solution to be determined and comparing its color with that of a definite amount of a standard solution of titanium similarly treated (Weller, Ber. Dtsch. chem. Ges. XV, 2592); (2) by reducing the titanium from the dioxide to the sesquioxide condition, by the use of zinc and hydrochloric acid, and then oxidizing it with permanganate (Osborn, Amer. Jour. Sci. [3] XXX, 329).

Separation. The general method for the separation of titanium from the other members of the aluminum group is to boil dilute acidified solutions (*vid.* Gravimetric Estimation). The titanium precipitate, however, carries down traces of other elements, as aluminum and iron.

From iron titanium may be separated (1) by passing hydrogen sulphide into an alkaline solution to which ammonium tartrate has been added,—the iron sulphide being precipitated (Gooch, Amer. Chem. Jour. VII, 283); (2) by treating a mixture of ferrous sulphide and titanic acid with sulphur dioxide (*vid.* Extraction); (3) by boiling a neutral solution with hydrogen dioxide,—metatitanic acid

being precipitated; (4) by treating a solution of the salts with phenylhydrazine,—titanic acid being precipitated (Allen, Jour. Amer. Chem. Soc. XXV, 421).

From aluminum titanium may be separated by boiling a solution containing them, in the presence of an alkali acetate and of acetic acid to about seven per cent. of the whole solution,—titanium basic acetate being precipitated (Gooch, Amer. Chem. Jour. VII, 283).

From cerium and thorium titanium may be separated by precipitating the double sulphates of those elements with potassium sulphate. Methods for the separation from zirconium have already been given (*vid.* Zirconium). From niobium and tantalum titanium may be separated by repeated fusions with acid potassium sulphate and extractions of the melt with water,—the titanium being in soluble form.

EXPERIMENTAL WORK ON TITANIUM.

Experiment 63. *Extraction of titanium salts from rutile.* (*a*) Mix 5 grm. of finely powdered mineral with about 30 grm. of acid potassium sulphate and fuse until the mass is free from black particles. Pulverize the fused mass and extract with cold water, stirring frequently until solution is complete. Add ammonium sulphide, filter and wash. Suspend the precipitate, which consists mainly of titanium hydroxide and ferrous sulphide, in water and pass a current of sulphur dioxide through the liquid until the ferrous sulphide has dissolved, as shown by the disappearance of the dark color. Filter, and wash the titanium hydroxide which remains.

(*b*) *Alternative method.* After having dissolved the fused mass in cold water (*vid.* (*a*)) add about 20 grm. of tartaric acid to hold up the titanium hydroxide, and make the solution faintly ammoniacal. Pass hydrogen sulphide through until the ferrous sulphide is completely thrown down. Filter, add

about 10 cm.^{3} of concentrated sulphuric acid to the filtrate, and evaporate in a porcelain dish under a draught hood until the tartaric acid is thoroughly carbonized. Allow the mass to stand until cool, add water, keeping the liquid cool to prevent the precipitation of the titanium hydroxide, and decant from the carbon residue. Filter the brown liquid through animal charcoal that is free from phosphates and precipitate the titanium hydroxide with ammonium hydroxide (R. G. Van Name).

Experiment 64. *Precipitation of titanium hydroxide,* ($Ti(OH)_4$). (*a*) To a solution containing titanium add sodium, potassium, or ammonium hydroxide. Note the comparative insolubility in excess, especially in ammonium hydroxide.

(*b*) Repeat the experiment, using the alkali carbonates. The precipitate is the same as in (*a*).

(*c*) Note the solubility of the freshly precipitated hydroxide in the common acids.

(*d*) Ignite a portion of the precipitate and try its solubility in acids.

Experiment 65. *Precipitation of titanic hydroxide or acid by boiling.* (*a*) Boil a dilute acid solution of titanic hydroxide. Note the precipitation. Filter, and test the filtrate with ammonium hydroxide.

(*b*) To a solution of titanic acid containing enough free acid to prevent precipitation on boiling, add ammonium acetate. Try similarly sodium thiosulphate.

Experiment 66. *Color tests of solutions containing titanium.* (*a*) To an acid solution containing titanium add hydrogen dioxide. Note the yellow color (TiO_3 in solution).

(*b*) To a solution containing titanium add a piece of metallic zinc and enough acid to start the action. Note the violet color which develops.

(*c*) To three portions of dry titanium oxide (TiO_2)

or double fluoride (K_2TiF_6) add a few drops of strong sulphuric acid. Bring into contact with the first a few particles of tannic acid, with the second a little dry pyrogallic acid, and with the third some morphia. Note the red color.

Experiment 67. *Negative test of titanium compounds.* Pass hydrogen sulphide through a solution containing titanium. Note the absence of precipitation.

NIOBIUM (COLUMBIUM), Nb(Cb), 94; TANTALUM, Ta, 183.

Discovery. Hatchett, while working with some chromium minerals in the British Museum in 1801, came across a black mineral very similar to those upon which he was engaged (Phil. Trans. Roy. Soc. (1802), 49). He obtained permission to examine it and found it to consist almost wholly of iron and an earth which did not conform to any known test. He described it as "a white, tasteless earth, insoluble in hot and cold water, acid to litmus, infusible before the blowpipe, and not dissolved by borax." The only acid which dissolved it was sulphuric. Since the mineral was of American origin, coming from Connecticut, the discoverer named it Columbite, and the element Columbium.

About a year later Ekeberg (Crell Annal. (1803) I, 3), while investigating a mineral from Kimito, Finland, which closely resembled columbite, discovered a "metal" which resembled tin, tungsten, and titanium. It proved to be none of these, but in fact a new element. He named it Tantalum, "because even when in the midst of acid it was unable to take the liquid to itself." Indeed, insolubility in acid seemed to be the chief characteristic of the new substance.

The apparent similarity of columbium and tantalum suggested that they might be identical, and in order to

solve this problem Wollaston (Phil. Trans. Roy. Soc. XCIX, 246) in 1809 began to work on tantalite and a specimen of the same columbite that Hatchett had examined. He found that the freshly precipitated acids were both soluble in concentrated mineral acids; if they were dried it was necessary to fuse them both with caustic alkalies before they could be dissolved. Both were held up if ammonium hydroxide was added in the presence of citric, tartaric, or oxalic acid. Having found practically the same reactions with both acids, he concluded that the elementary substances were the same. The specific gravity of tantalite, however, was 7.95, and that of columbite 5.91. This he explained by suggesting different conditions of oxidation or different states of molecular structure. These conclusions were accepted, and for many years the element was called indifferently tantalum and columbium.

In 1844 Rose began to investigate the same subject. His work on the columbites of Bodenmais and Finland led him to the belief that there were two distinct acids in the columbite from Bodenmais, one similar to that in tantalite, the other containing a new element, to which he gave the name Niobium, from Niobe, daughter of Tantalus. Though niobium proved to be Hatchett's columbium, Rose's name for the element has been the one more generally adopted.

Occurrence. Niobium and tantalum are found, each in combination, in various rare minerals. They usually, though not invariably, occur together.

	Contains Nb_2O_5	Contains Ta_2O_5
Pyrochlore, $RNb_2O_6 \cdot R(Ti,Th)O_3$	47–58%	
Koppite, $R_2Nb_2O_7 \cdot \frac{2}{5}NaF$	61–62%	
Hatchettolite, $2R(Nb,Ta)_2O_6 \cdot R_2(Nb,Ta)_2O_7$	63–67%*	

* $Nb_2O_5 + Ta_2O_5$.

	Contains Nb_2O_5	Ta_2O_5
Microlite, $Ca_2Ta_2O_7$.	7– 8%	68–69%
Fergusonite, (Y,Er,Ce)(Nb,Ta)O_4.	14–46%	4–43%
Sipylite, $\overset{III}{R}NbO_4$.	47–48%	1– 2%
Columbite, (Fe,Mn)$(Nb,Ta)_2O_6$.	26–77%	1–77%
Tantalite, $FeTa_2O_6$.	3–40%	42–84%
Skogbölite, "	3–40%	42–84%
Tapiolite, $Fe(Nb,Ta)_2O_6$.	11–12%	73–74%
Mossite, $Fe(Nb,Ta)_2O_6$.	83%*	
Yttrotantalite, $\overset{II}{R}\overset{III}{R}_2(Ta,Nb)_4O_{15}$.	12–13%	46–47%
Samarskite, $\overset{III}{R}_2\overset{II}{R}_3(Nb,Ta)_6O_{21}$.	41–56%	14–18%
Stibiotantalite, $Sb_2O_3(Ta,Nb)_2O_5$?.	7·5 %	51%
Ånnerödite, complex.	48–49%	
Hielmite, complex.	4–16%	55–72%
Æschynite, $\overset{III}{R}_2Nb_4O_{13}\cdot\overset{III}{R}_2(Ti,Th)_5O_{13}$.	32–33%	21–22%
Polymignite, $5RTiO_3\cdot 5RZrO_3\cdot R(Nb,Ta)_2O_6$.	11–12%	1– 2%
Euxenite, $\overset{III}{R}(NbO_3)_3\cdot\overset{III}{R}_2(TiO_3)_3\cdot\frac{3}{2}H_2O$.	18–35%	
Polycrase, $\overset{III}{R}(NbO_3)_3\cdot 2\overset{III}{R}_2(TiO_3)_3\cdot 3H_2O$.	19–25%	0– 4%
Wöhlerite, $12R(Si,Zr)O_3\cdot RNb_2O_6$.	12–14%	
Låvenite, $R(Si,Zr)O_3\cdot Zr(SiO_3)_2\cdot RTa_2O_6$.	0– 5%*	
Dysanalyte, $6RTiO_3\cdot RNb_2O_6$.	0–23%	0– 5%
Eucolite, complex silicates.	2– 4%*	
Melanocerite, complex silicates.		3– 4%
Tritomite, complex silicates.		1– 3%
Cassiterite (ainalite), SnO_2.		0– 9%

Extraction. Salts of niobium and tantalum may be extracted from columbite or tantalite by either of the following methods:

* $Nb_2O_5 + Ta_2O_5$.

(1) The mineral is fused with six parts of potassium bisulphate, the fused mass is pulverized and treated with hot water and dilute hydrochloric acid. The residue is then digested with ammonium sulphide to remove tin, tungsten, etc., and again warmed with dilute hydrochloric acid. After this treatment it is washed thoroughly with water and dissolved in hydrofluoric acid. Filtration is followed by the addition of potassium carbonate to the clear solution until a precipitate begins to form. The potassium and tantalum double fluoride separates first in needle-like crystals, after which the niobium oxyfluoride crystallizes in plates.

(2) The mineral is fused with three parts of acid potassium fluoride (*vid.* Experiment 68).

The Elements. I. NIOBIUM. *A. Preparation.* The element niobium may be obtained by reducing the chloride with hydrogen at a high temperature (Bloomstrand).

B. Properties. Niobium is a metallic element of steel-gray color and brilliant luster. Heated in the air it ignites; heated in chlorine it forms the chloride ($NbCl_5$). It is very slightly soluble in hydrochloric acid, nitric acid, and aqua regia, but dissolves in concentrated sulphuric acid upon the application of heat. Its specific gravity is 7.06.

II. TANTALUM. *A. Preparation.* Elementary tantalum may be obtained by heating the potassium and tantalum fluoride (K_2TaF_7) with potassium and extracting the potassium fluoride with water.

B. Properties. Tantalum in the elementary condition is a black substance with a metallic luster. Like niobium it ignites when heated in the air and forms the chloride, ($TaCl_5$), when heated in chlorine. It is insoluble in hydrochloric, nitric, and sulphuric acids, and in aqua regia, but dissolves in hydrofluoric acid. Its specific gravity is 10.78.

Compounds. *A. Typical forms.* The following are typical compounds of niobium and tantalum:

Oxides..........	Nb_2O_3	
	Nb_2O_4	Ta_2O_4
	Nb_2O_5	Ta_2O_5
Chlorides........	$NbCl_3$	
	$NbCl_5$	$TaCl_5$
Oxychloride.....	$NbOCl_3$	
Bromides.......	$NbBr_5$	$TaBr_5$
Oxybromide....	$NbOBr_3$	
Fluorides.......	NbF_5	TaF_5
Oxyfluoride.....	$NbOF_3$	
Fluotantalates ..		K_2TaF_7
		Na_2TaF_7
		$(NH_4)_2TaF_7$
Double fluorides.	$xKF \cdot yNbOF_3$, $xKF \cdot yNbO_2F$ (typical)	
Sulphide........		Ta_2S_4
Oxysulphide....	Nb_2OS_3	
Nitride.........		Ta_3N_5
Niobates........	$K_8Nb_6O_{19} + 16H_2O$	
	$K_6Nb_4O_{13} + 13H_2O$	
	$2K_2Nb_4O_{11} + 11H_2O$	
	$K_4Nb_2O_7 + 11H_2O$	
	$Na_{16}Nb_{14}O_{43}$	
	$Na_2Nb_2O_6$, etc.	
Tantalates......		Of types $\overset{I}{R}_8Ta_6O_{19}$ and $RTaO_3$, with Na, K, NH_4, Ba, and Mg.

B. Characteristics. The compounds of niobium closely resemble those of tantalum, both in chemical form and in behavior toward reagents. The two elements are closely associated in minerals (*vid.* Occurrence). The lower oxides of niobium are dark powders which oxidize when heated. The dioxide is soluble in hydrochloric acid, while the tetroxide is not attacked by acids. The pentoxide is a yellowish-white amorphous powder somewhat soluble in concentrated sulphuric acid before ignition, but insoluble after.

Niobium pentachloride is a yellow crystalline substance which tends to form the oxychloride in the presence of water, and is reduced to the trichloride when its vapor is passed through a red-hot tube. The fluoride is formed by the action of hydrofluoric acid upon the pentoxide.

Tantalum tetroxide is a very hard, dark-gray, porous mass which is not attacked by acids. When heated it goes over to the higher oxide. The pentoxide of tantalum is a white powder which is somewhat soluble in acids. The chloride and fluoride of tantalum are formed similarly to the corresponding salts of niobium and resemble them in general behavior. Niobates and tantalates are obtained by fusing the oxides with caustic alkalies; these salts are soluble. The tantalum compounds give no color test with morphia, tannic acid, or pyrogallic acid.

Estimation. *A. Gravimetric.* Niobium and tantalum are ordinarily weighed as the oxides Nb_2O_5 and Ta_2O_5, obtained from ignition of the acids.

B. Volumetric. Niobium may be estimated volumetrically by reduction from the condition of the pentoxide to that of the trioxide by means of zinc and hydrochloric acid in a current of carbon dioxide, and oxidation with permanganate (Osborn, Amer. Jour. Sci. [3] xxx, 329).

Separation. The method usually employed for the separation of niobium and tantalum from the elements with which they are generally associated—namely, titanium, zirconium, and thorium—is that of fusion with acid potassium sulphate (*vid.* Titanium). From tin and tungsten they may be separated by ammonium sulphide.

The separation of niobium from tantalum is one of the most difficult of analytical problems. Marignac's method (Ann. Chim. Phys. [4] VIII, 1), based upon the difference in solubility * between the tantalum-potassium

* K_2TaF_7 is soluble in 151–157 parts of cold water. $2KF \cdot NbOF_3 + H_2O$ is soluble in 12–13 parts of cold water.

fluoride (K_2TaF_7) and the niobium-potassium oxyfluoride ($2KF \cdot NbOF_3 + H_2O$), is the most satisfactory known.

EXPERIMENTAL WORK ON NIOBIUM AND TANTALUM.

Experiment 68. *Extraction of niobium and tantalum salts from columbite or tantalite.* Mix 5 grm. of the finely ground mineral with 15 grm. of acid potassium fluoride and fuse thoroughly. Pulverize the fused mass and extract with boiling water containing a little hydrofluoric acid. Evaporate to about 200 cm.^{3} and allow the liquid to stand. The potassium and tantalum fluoride separates first in needle-like form; the niobium and potassium oxyfluoride crystallizes in plates on concentration of the solution. The salts of the two elements should be purified as far as possible by fractional crystallizations.

Experiment 69. *Preparation of niobic and tantalic oxides* (*acids*), (Nb_2O_5; Ta_2O_5). (*a*) Evaporate a solution of potassium and niobium oxyfluoride to dryness, add strong sulphuric acid, and heat until all the hydrofluoric acid is expelled and a solution is obtained. Cool the solution, dilute with water, and boil. Niobic acid, (Nb_2O_5), is precipitated. Filter, and test the filtrate with ammonium hydroxide.

(*b*) Repeat the experiment, using a solution of potassium and tantalum fluoride instead of the niobium salt.

(*c*) Test the action of alkali hydroxides or carbonates in excess upon solutions of niobium and tantalum obtained in (*a*) and (*b*).

Experiment 70. *Action of fusion with sodium or potassium hydroxide upon niobic and tantalic acids.* (*a*) Melt a gram of sodium or potassium hydroxide in a hard glass tube, add a small quantity of dry niobic acid, and heat again. Note that the fused mass is soluble in water.

(*b*) Repeat the experiment, using dry tantalic acid instead of niobic.

(*c*) Acidify portions of the solutions obtained in (*a*) and (*b*).

Experiment 71. *Color tests for niobium.* (*a*) Treat separate portions of dry niobic oxide (or acid) with tannic acid, pyrogallic acid, and morphia, as in Experiment 66 (*c*). Note the brown color.

(*b*) Repeat the experiment, using tantalic oxide instead of niobic. Note the absence of color.

(*c*) Try the action of metallic zinc upon an acid solution containing niobium.

Experiment 72. *Negative tests of niobium and tantalum.* Note that hydrogen sulphide gives no precipitate, and that hydrogen peroxide gives no yellow color with acid solutions containing niobium or tantalum.

INDIUM, In, 114.

Discovery. Indium was discovered by Reich and Richter in 1863, in the course of an examination of two ores consisting mainly of the sulphides of arsenic, zinc, and lead (J. pr. Chem. LXXXIX, 441). These ores had been freed from the greater part of their arsenic and sulphur by roasting, and the residue had been evaporated to dryness with hydrochloric acid and distilled. The crude chloride of zinc thus obtained was examined with the spectroscope for thallium, since the presence of that element had been indicated in similar ores from the Freiberg mines. Instead of the thallium line, however, appeared one of indigo blue never before observed. The color suggested the name Indium for the unknown element present.

Occurrence. Indium occurs in very small amounts, combined with sulphur, in many zinc-blendes. It has been found in zinc-blende from Freiberg and Breitenbrun in

Saxony, and from Schönfeld in Bohemia; in christophite, a variety of zinc-blende; in zinc prepared from these ores; and in the flue-dust from ovens used for roasting zinc ores. It has also been found in wolframite from Zinnwald. The proportion of indium in the minerals named varies from one tenth of one per cent. to mere traces. Lockyer detected it in the atmosphere of the sun. Hartley and Ramage (Jour. London Chem. Soc. (1897), 533, 547) have discovered it spectroscopically in many iron ores,—notably siderites,—in some manganese ores, in zinc-blendes, in five tin ores examined, and in many pyrites.

Extraction. Indium salts may be obtained as follows from zinc that has been extracted from indium-bearing blendes. The crude metal is nearly dissolved in hydrochloric or nitric acid, and the solution is allowed to stand twenty-four hours with the undissolved metal. A spongy mass, consisting of the indium together with lead, copper, cadmium, tin, arsenic, and iron, collects upon the residual zinc. This mass is washed with water containing some sulphuric acid; it is then dissolved in nitric acid and evaporated with sulphuric acid until all the nitric acid is removed. By this process the lead is precipitated, and it may be removed by filtration. The solution that remains is treated with ammonium hydroxide in excess, and the hydroxides of iron and indium are filtered off and dissolved in a small amount of hydrochloric acid. This solution is treated with an excess of acid sodium sulphite and boiled. Indium is precipitated as the basic sulphite ($In_2(SO_3)_3 \cdot In_2(OH)_6 + 5H_2O$).

The Element. *A. Preparation.* Elementary indium may be obtained (1) by heating the oxide with carbon or in a current of hydrogen; (2) by heating the oxide with sodium under a layer of dry sodium chloride; (3) by treating the salts with zinc.

B. Properties. Indium is a soft white metal, less vola-

tile than cadmium and zinc. It melts at 174° C. At ordinary temperatures it is very stable in the air, but when heated it ignites and burns with a violet flame to the oxide. It does not decompose boiling water. It dissolves easily in hydrochloric, nitric, and sulphuric acids. Its specific gravity is given at from 7.1 to 7.4.

Compounds. *A. Typical forms.* The following compounds of indium are known:

Oxides	InO	In_2O_3
Hydroxide		$In(OH)_3$
Chlorides	$InCl$ $InCl_2$	$InCl_3$
Indium-hydrochloric acid		H_3InCl_6
Bromide		$InBr_3$
Iodide		InI_3
Nitrate		$In_2(NO_3)_6+9H_2O$
Sulphate		$In_2(SO_4)_3$
Double sulphates		$In_2(SO_4)_3 \cdot K_2SO_4+24H_2O$; $In_2(SO_4)_3 \cdot (NH_4)_2SO_4+24H_2O$
Sulphite		$In_2(SO_3)_3 \cdot In_2(OH)_6+5H_2O$
Sulphide		In_2S_3
Sulpho salts		$K_2In_2S_4$; $Na_2In_2S_4$

B. Characteristics. Indium resembles aluminum in forming alums with potassium and ammonium sulphates, and in having a hydroxide soluble in excess of potassium or sodium hydroxide. It resembles zinc in forming a sulphide with hydrogen sulphide, but in the case of indium this salt is yellow. Indium monoxide is a dark powder slowly soluble in dilute acids. The sesquioxide is a yellowish-white powder easily soluble in warm acid. The dichloride is formed directly by the union of chlorine with the metal, and is a white, crystalline mass. In water it separates into the trichloride and the metal. By fusion of

the dichloride with elementary indium the monochloride is formed,—a reddish-black, crystalline substance. The trichloride is formed also by the action of chlorine in excess upon the metal; it is white like the dichloride and dissolves in water with the evolution of heat. Solutions of indium salts color the flame violet and give a characteristic flame spectrum.

Estimation. Indium is generally determined as the oxide, (In_2O_3), obtained by ignition of the hydroxide, or as the sulphide, (In_2S_3), obtained by precipitation with hydrogen sulphide in the presence of sodium acetate.

Separation. The separation of this very rare element from those elements with which it is usually associated is treated under Extraction.

GALLIUM, Ga, 70.

Discovery. In 1875 Lecoq de Boisbaudran, who had done much work with spectrum analysis, notified the Académie des Sciences of his discovery of a new element in a zinc-blende from the mine of Pierrefitte in the Pyrenees, and proposed for it the name Gallium (Compt. rend. LXXXI, 493; Chem. News XXXII, 159). The individuality of the new body was distinctly indicated by the spectroscope, but so small was the amount of it in the possession of the discoverer that few of its reactions were determined. Among the properties which he described, however, were the following: the oxide, or perhaps a subsalt, was thrown down by metallic zinc in a solution containing chlorides and sulphates; in a mixture containing an excess of zinc chloride the new body was the first to be precipitated by ammonia; in the presence of zinc it was concentrated in the first sulphides deposited; the spark spectrum of the concentrated chloride showed two violet lines, one of them of considerable brilliance.

Occurrence. Gallium is found combined, in very small amounts, in certain minerals, chiefly zinc-blendes from Bensberg on the Rhine, Pierrefitte, and other localities. It has been detected in some American zinc-blendes (Chem. Ztg. (1880), 443). The Bensberg sphalerite, one of the richest sources, contains 0.016 grm. per kilo.

Hartley and Ramage obtained the following interesting results by means of the spectroscope (Jour. London Chem. Soc. (1897), 533, 547): the presence of gallium was indicated in thirty-five out of ninety-one iron ores examined; in all the magnetites, seven in number; in all the aluminum ores, fifteen in number, mostly kaolin and bauxite; in four out of twelve manganese ores; and in twelve out of fourteen zinc-blendes.

Extraction. Salts of gallium are obtained by the following process: The mineral is dissolved in aqua regia and the excess of acid expelled by boiling. When the solution is cold, pure zinc is added, which precipitates the antimony, arsenic, bismuth, copper, cadmium, gold, lead, mercury, silver, tin, selenium, tellurium, and indium. These are filtered off while there is still some evolution of hydrogen, and the filtrate is boiled from six to twenty-four hours with metallic zinc. Gallium is precipitated as a basic salt, together with salts of aluminum, iron, zinc, etc. To obtain the gallium salt in a more nearly pure condition the precipitate is dissolved in hydrochloric acid, the solution is treated with hydrogen sulphide, and after filtration and the removal of the excess of hydrogen sulphide by boiling, sodium carbonate is added in small portions. The gallium salt is the first to be precipitated, and the precipitates are collected as long as they show the gallium lines in the spark spectrum. These precipitates are dissolved in sulphuric acid and the solution is diluted largely with water and boiled. The basic sulphate of gallium which is thus thrown down is dissolved in sulphuric acid,

and potassium hydroxide is added in excess. Iron if present is removed at this point by filtration and the gallium oxide is then precipitated from the filtrate by carbon dioxide.

The Element. *A. Preparation.* Gallium in the elementary condition has been obtained by subjecting an alkaline solution of the oxide to electrolysis.

B. Properties. A gray, lustrous metal, showing greenish-blue lights on reflecting surfaces, gallium is malleable and fairly hard. Its fusing point, 30.15° C., is so low that it melts readily from the warmth of the hand. In water, and in air at ordinary temperatures, it is unchanged; when heated in air or oxygen it is oxidized only superficially. It combines rapidly with chlorine, more slowly with bromine, and not at all with iodine unless heat is applied. Gallium is soluble in hydrochloric and warm nitric acids, and somewhat soluble in potash and ammonia solutions. It alloys easily with aluminum, and these alloys decompose cold water rapidly. Its specific gravity is 6.

Compounds. *A. Typical forms.* The following compounds of gallium are known:

Oxides	GaO?	Ga_2O_3
Hydroxide		$Ga(OH)_3$?
Chlorides	$GaCl_2$	$GaCl_3$
Bromide		$GaBr_3$
Iodide		GaI_3
Nitrate		$Ga_2(NO_3)_6$
Sulphate		$Ga_2(SO_4)_3$
Double sulphate		$Ga_2(SO_4)_3 \cdot (NH_4)_2SO_4 + 24H_2O$

B. Characteristics. The compounds of gallium resemble those of aluminum and indium in forming alums and in having a hydroxide soluble in excess of sodium or potassium hydroxide. The salts are colorless, and in dilute solutions tend, on being heated, to become basic

and separate from the solution. The oxide (Ga_2O_3) is insoluble in acids and alkalies after ignition.

Estimation. Gallium is usually weighed as the oxide (Ga_2O_3).

Separation.* *Vid.* Extraction.

THALLIUM, Tl, 204.1.

Discovery. Some years previous to 1861 Crookes had been engaged in the extraction of selenium from a seleniferous deposit which he had obtained from the sulphuric-acid manufactory at Tilkerode in the Hartz Mountains. Some residues, left after the purification of the selenium, and supposed to contain tellurium, were set aside and not examined until 1861, when, needing tellurium, Crookes vainly tried to isolate it by various chemical methods. At length he resorted to spectrum analysis and tested some of the residue in the flame. The spectrum of selenium appeared, and as it was fading, and he was looking for evidence of tellurium, a new bright-green line flashed into view. The element whose presence was thus indicated received the name Thallium, from the Greek θαλλός, or the Latin *thallus, a budding twig* (Chem. News III, 194).

About the same time Lamy announced the discovery of the same element (Ann. Chim. Phys. [3] LXVII, 385), but after much discussion and the presentation of much evidence on both sides it was declared that Crookes had the priority of discovery.

Occurrence. Thallium occurs in certain very rare minerals:

Crookesite, $(Cu,Tl,Ag)_2Se$, contains 16–19% Tl
Lorandite, $TlAsS_2$, " 59–60% Tl

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* For a detailed study of the separation of gallium, see many articles by Lecoq de Boisbaudran, Compt. rend. XCIV–XCVIII.

It is found also in very small quantities in berzelianite, (Cu_2Se); in some zinc-blendes and copper pyrites; in iron pyrites from Theux, Namur, Philippeville, Alais, and Nantes; in lepidolite from Mähren; and in mica from Zinnwald. It has been detected, together with cæsium, rubidium, and potassium, in the mineral waters of Nauheim and Orb. Its presence in the flue-dust from some iron furnaces and sulphuric-acid works, as well as in some crude sulphuric and hydrochloric acids, may be traced to its presence in the pyrites used.

Extraction. Thallium salts may be extracted by the following methods:

(1) *From minerals.* The finely powdered mineral is dissolved in aqua regia. The solution is evaporated with sulphuric acid until the free acid has been removed; it is then diluted abundantly with water, neutralized with sodium carbonate, and treated with potassium cyanide in excess. This precipitates the bismuth and lead, which are filtered off. The filtrate is treated with hydrogen sulphide, which precipitates the cadmium, mercury, and thallium as the sulphides. Very dilute sulphuric acid dissolves the thallium sulphide, leaving the cadmium and mercury sulphides undissolved (Crookes).

(2) *From flue-dust.* The material is treated with an equal weight of boiling water in a large wooden tub, and is allowed to stand twenty-four hours. The liquid is siphoned off and is precipitated with hydrochloric acid.* The crude chloride thus obtained is treated with an equal weight of sulphuric acid, and heated to expel the hydrochloric acid and the greater part of the excess of sulphuric. The sulphate obtained is dissolved in water, the solution is neutralized with chalk and filtered. By the addition of hydrochloric acid to the filtrate, nearly pure thallous chloride is precipitated (Chem. News VIII, 159).

* Three tons of dust gave sixty-eight pounds of crude thallous chloride.

The Element. *A. Preparation.* The element thallium may be obtained (1) by fusing a mixture of thallous chloride and sodium carbonate with potassium cyanide; (2) by submitting the carbonate or the sulphate to electrolysis; (3) by heating the oxalate; and (4) by precipitating with zinc from an alkaline solution of a thallous salt.

B. Properties. Metallic thallium is in color whitish to blue gray, with the luster of lead. It is soft and malleable and melts at 285° C. It oxidizes readily at high temperatures, but is not acted upon by water free from air. It is soluble in dilute nitric and sulphuric acids. It is a poor conductor of electricity. The specific gravity of thallium is 11.88.

Compounds. *A. Typical forms.* The following are typical compounds of thallium:

Oxides	Tl_2O	Tl_2O_3
Hydroxides	$TlOH$	$Tl(OH)_3$
Carbonate	Tl_2CO_3	
Chlorides	$TlCl$	$TlCl_3 + H_2O$
Double chlorides	$TlCl \cdot HgCl_2$; $3TlCl \cdot FeCl_3$; $TlCl \cdot AuCl_3$; etc.	$TlCl_3 \cdot 3KCl + 2H_2O$; etc.
Chlorate	$TlClO_3$	
Perchlorate	$TlClO_4$	
Bromides	$TlBr$	$TlBr_3$
Double bromides		$TlBr_3 \cdot KBr + 2H_2O$; $TlBr_3 \cdot 3TlBr$
Bromate	$TlBrO_3$	
Iodides	TlI	TlI_3
Double iodides	$TlI \cdot KI$	$TlI_3 \cdot NH_4I$
Iodates	$TlIO_3$	$Tl(IO_3)_3$
Periodate		$3Tl_2O_3 \cdot I_2O_7 + 30H_2O$
Thiosulphate	$Tl_2S_2O_3$	
Sulphides	Tl_2S	Tl_2S_3
Sulphite	Tl_2SO_3	
Sulphates	Tl_2SO_4; $TlHSO_4$	$Tl_2(SO_4)_3$
Double sulphates	with $MgSO_4$, $ZnSO_4$, $CuSO_4$, etc.	
Alums	$Tl_2SO_4 \cdot Al_2(SO_4)_3 + 24H_2O$; $Tl_2SO_4 \cdot Fe_2(SO_4)_3 + 24H_2O$	
Nitrates	$TlNO_3$	$Tl(NO_3)_3 + 4H_2O$
Phosphates	Tl_3PO_4; $Tl_4P_2O_7$; $TlPO_3$	$TlPO_4 + 2H_2O$

Arseniates........	Tl_3AsO_4	$TlAsO_4 + 2H_2O$
Cyanides.........	$TlCN$	$Tl(CN)_3 \cdot TlCN$
Sulphocyanide....	$TlSCN$	
Ferrocyanide.....	$Tl_4Fe(CN)_6 + 2H_2O$	
Silicofluoride.....	Tl_2SiF_6	
Chromates........	Tl_2CrO_4; $Tl_2Cr_2O_7$	
Chloroplatinate...	Tl_2PtCl_6	
Molybdate........	Tl_2MoO_4	
Tungstate........	Tl_2WO_4	
Vanadates........	Tl_3VO_4; $Tl_4V_2O_7$; $TlVO_3$	

B. Characteristics. Thallium compounds are known in two conditions of oxidation, the thallous, (Tl_2O), and the thallic, (Tl_2O_3). The lower condition is the more stable; consequently the thallous compounds are the more numerous and the better known. When the metal is allowed to oxidize in the air it forms the thallous oxide, but when it is melted in an atmosphere of oxygen, thallic oxide is obtained. Thallic chloride, bromide, and iodide may be formed by treating the corresponding thallous salts with an excess of chlorine, bromine, and iodine, respectively. In general, the thallous salts may be oxidized to the thallic form by strong oxidizing agents, such as potassium permanganate, lead dioxide, barium dioxide, etc. Thallium in the lower condition resembles the alkalies potassium, cæsium, and rubidium in having a soluble hydroxide, carbonate, and sulphate, and an insoluble chloroplatinate; also in forming alums. It resembles lead in forming an insoluble sulphide and chromate, and in having halogen salts soluble in hot water. The thallous salts are colorless when the base is combined with a colorless acid. The sulphide is brownish black. The thallic salts are in general unstable, and on being heated with water tend to precipitate the oxide ($Tl_2O_3 \cdot H_2O$). They may be easily reduced to the lower condition by the action of reducing agents. They may be formed by the careful treatment of thallic oxide with acids, as well as by the action of strong oxidizing agents upon the thallous salts. Solutions of thallium

salts in either condition of oxidation give to the flame a characteristic green color.

Estimation.* *A. Gravimetric.* Thallium is generally weighed in the thallous condition (1) as the chloroplatinate, (Tl_2PtCl_6), after precipitation by chloroplatinic acid (Crookes, Select Methods, Second Edition, 380); (2) as the iodide (TlI), after precipitation by potassium iodide (Werther, Zeitsch. anal. Chem. III, 1, and J. B. (1864), 712; Long, Zeitsch. anal. Chem. XXX, 342); (3) as the chromate (Tl_2CrO_4), after precipitation in alkaline solution by potassium chromate (Browning and Hutchins, Amer. Jour. Sci. [4] VIII, 460); (4) as the sulphate (Tl_2SO_4), after evaporation of appropriate salts with sulphuric acid in excess and ignition at low red heat, or as the acid sulphate, ($TlHSO_4$), obtained by substituting for ignition heating at 220°–240° C. (Browning, Amer. Jour. Sci. [4] IX, 137).

B. Volumetric. Thallium is estimated volumetrically (1) by the oxidation of thallous salts with permanganate (Crookes, Select Methods, Second Edition, 381); (2) by the action of potassium iodide upon thallic salts, as shown in the following equation (Thomas, Compt. rend. CXXXIV, 655): $TlCl_3 + 3KI = TlI + 3KCl_3 + I_2$.

Separation.† In the more stable thallous condition, to which thallic salts may readily be reduced, thallium may be separated as follows: from the metals which give precipitates with hydrogen sulphide in acid (but not acetic) solution, by hydrogen sulphide; from elements which form insoluble hydroxides with the alkali hydroxides, by these reagents; and from the alkalies and alkali earths, by ammonium sulphide.

* See also Hebberling, Liebig Annal. CXXXV, 207; Phipson, Compt. rend. LXXVIII, 563; Neumann, Liebig Annal. CCXLIV, 349; Feit, Zeitsch. anal. Chem. XXVIII, 314; Carnot, Compt. rend. CIX, 177; Sponholz, Zeitsch. anal. Chem. XXXI, 519; Thomas, Compt. rend. CXXX, 1316; Marshall, Jour. Soc. Chem. Ind. XIX, 994.

† See Crookes, Select Methods, Second Edition, 382–386.

EXPERIMENTAL WORK ON THALLIUM.

Experiment 73. *Extraction of thallium salts from flue-dust.* The method described under Extraction may be followed.

Experiment 74. *Precipitation of thallous chloride, bromide, and iodide* ($TlCl$; $TlBr$; TlI). (*a*) To a solution of a thallous salt add hydrochloric acid or a chloride in solution. Note the solvent action of boiling water. Try the effect of cooling the hot solution.

(*b*) Repeat the experiment, using potassium bromide as the precipitant.

(*c*) Try similarly potassium iodide.

Experiment 75. *Precipitation of thallium chloroplatinate* (Tl_2PtCl_6). To a solution of a thallous salt add a few drops of a solution of chloroplatinic acid.

Experiment 76. *Precipitation of thallous chromate* (Tl_2CrO_4). To a solution of a thallous salt add some potassium chromate in solution. Try the action of acids upon the precipitate.

Experiment 77. *Precipitation of thallous sulphide* (Tl_2S). (*a*) Through a solution of a thallous salt acidified with dilute sulphuric acid pass hydrogen sulphide. Note the absence of precipitation. Divide the solution, and to one part add ammonium acetate and to the other ammonium hydroxide.

(*b*) Try the action of ammonium sulphide upon a thallous salt in solution.

Experiment 78. *Oxidation of thallous salts.* (*a*) To a solution of a thallous salt acidified with sulphuric acid add gradually a little potassium permanganate. Note the disappearance of the color of the permanganate.

(*b*) To a solution of a thallous salt add bromine water until the color of the bromine ceases to fade. To one portion add a few drops of a solution of a chloride or bro-

mide. Note the absence of precipitation. To another portion add sodium or potassium hydroxide. Note the precipitation of brown thallic hydroxide, ($Tl_2O_3 \cdot H_2O$).

Experiment 79. *Reduction of a thallic salt.* To a solution of a thallic salt formed, for example, as in Experiment 78 (*b*) add stannous chloride. Note the precipitation of thallous chloride, (TlCl).

Experiment 80. *Flame and spectroscopic tests for thallium salts.* (*a*) Dip the end of a platinum wire into a solution of a thallium salt and hold it in the flame of a Bunsen burner. Note the green color.

(*b*) Examine spectroscopically the flame colored by a solution of a thallium salt. Observe the green line.

Experiment 81. *Negative tests of thallous salts.* Note that sulphuric acid and the alkali hydroxides and carbonates give no precipitate with solutions of thallous salts.

VANADIUM, V, 51.2.

Discovery. As early as 1801 Del Rio announced the discovery of a new metal in a lead ore from Zimapan, Mexico. He named it Erythronium (ἐρυθρός, *red*), because its salts became red when heated with acids (Annal. der Phys. u. Chem. LXXI, 7). Fourteen years later Collet Descotils examined the supposed metal and pronounced it an impure oxide of chromium,—a conclusion that Del Rio himself came to accept (Ann. de Chim. LIII, 268).

In 1830 Sefström found an unknown metal in an iron ore from Taberg, Sweden. He proposed for it the name Vanadium, from Vanadis, the Scandinavian goddess more commonly known as Freia (Amer. Jour. Sci. [1] XX, 386). Almost immediately Wöhler showed the identity of vanadium with the metal described by Del Rio (Pogg. Annal. XXI, 49).

Occurrence. Vanadium is found quite widely distributed, but always in combination, and in very small quantities:

	Contains V_2O_5.
Vanadinite, $(PbCl)Pb_4(VO_4)_3$.	8–21%
Descloizite, $(Pb,Zn)_2(OH)VO_4$.	20–22%
Cuprodescloizite, $(Pb,Zn,Cu)_2(OH)VO_4$.	17–22%
Calciovolborthite, $(Cu,Ca)_2(OH)VO_4$.	37–39%
Carnotite, $K_2O \cdot 2U_2O_3 \cdot V_2O_5 \cdot 3H_2O$.	19–20%
Brackebuschite, formula doubtful.	24–25%
Psittacinite, formula doubtful.	17–26%
Volborthite, " "	14–15%
Pucherite, $BiVO_4$.	22–27%
Roscoelite, silicate, formula doubtful.	21–29%
Ardennite, " " "	traces – 9%

Vanadium has been detected also in some copper, lead, and iron ores, in certain clays and basalts, and sometimes in soda ash and phosphate of soda.

Extraction. Vanadium salts may be extracted from mineral sources by the following methods:

(1) The mineral is fused with potassium nitrate, and the potassium vanadate thus formed is extracted with water. By the addition of a soluble lead or barium salt to the solution the lead or barium vanadate is precipitated. This insoluble vanadate is decomposed by means of sulphuric acid, and the barium or lead sulphate is filtered off. By saturation of the filtrate with ammonium chloride the ammonium vanadate is precipitated.

(2) The finely ground mineral is decomposed by nitric acid (*vid.* Experiment 82).

The Element. *A. Preparation.* Elementary vanadium may be prepared by long heating of the dichloride in a current of hydrogen.

B. Properties. Vanadium is a non-magnetic, light-gray powder, somewhat crystalline in appearance. It oxidizes slowly in the air at ordinary temperatures, but more rapidly when heated, going through various degrees of oxidation and showing a characteristic color for each oxide,—brown (V_2O), gray (V_2O_2), black (V_2O_3), blue (V_2O_4), and red (V_2O_5). Upon the application of heat vanadium unites with chlorine, forming the chloride VCl_4; at a red heat it combines with nitrogen, giving the nitride VN. It is insoluble in hydrochloric and dilute sulphuric acids, and soluble in nitric, hydrofluoric, and concentrated sulphuric acids. It is not attacked by alkaline solutions, but with melted alkalies forms the alkali vanadates, with the evolution of hydrogen. The specific gravity of vanadium is 5.5.

Compounds. *A. Typical forms.* The following may be considered typical compounds of vanadium:

Oxides	V_2O	V_2O_2	V_2O_3	V_2O_4	V_2O_5
Chlorides		VCl_2	VCl_3	VCl_4	
Oxychlorides			$VOCl$	$VOCl_2$	
Bromide			VBr_3		
Oxybromides				$VOBr_2$	$VOBr_3$
Fluorides			$V_2F_6+6H_2O$		VF_5
Double fluorides			V_2F_6 with KF, CoF_2, NiF_2, etc.		
Sulphides		V_2S_2	V_2S_3		$V_2S_3O_2$
					V_2S_5
Sulpho salts					Na_3VS_3O
					$(NH_4)_3VS_4$, etc.
Sulphate					$V_2O_2(SO_4)_2$
Nitrides			VN		VN_2
Vanadates, ortho,					$\overset{I}{R}_3VO_4$
pyro,					$\overset{I}{R}_4V_2O_7$
meta,					$\overset{I}{R}VO_3$
complex, V_2O_5 with P_2O_5, MoO_3, WO_3, SiO_2, AsO_5, etc.					

B. Characteristics. The vanadium compounds are known in five conditions of oxidation, represented by the five oxides. Of these conditions the highest is the most

stable and is known in the largest number of salts, the vanadates. Vanadic pentoxide is reddish yellow in color, and, like phosphoric pentoxide, it dissolves readily in the alkali hydroxides and carbonates. The alkali vanadates thus formed are of the ortho, pyro, and meta types, ($\overset{I}{R}_3VO_4$; $\overset{I}{R}V_2O_7$; $\overset{I}{R}VO_3$). The vanadates are generally pale yellow in color. They are soluble in the stronger acids and with the exception of the alkali vanadates insoluble in water. Vanadic acid is easily reduced by reducing agents to the tetroxide condition, when the solution becomes blue. More powerful reducing agents carry the reduction further, to the trioxide, or even the dioxide condition, but only long-continued heating in a current of hydrogen brings about the reduction to the monoxide and the element.

Hydrogen sulphide, acting upon vanadic acid, reduces it to the tetroxide condition or even below, with a separation of sulphur. Ammonium sulphide gives the dark-brown solution of a sulpho salt, ($(NH_4)_3S_3VO$?), and this solution, when acidified, gives a brown oxysulphide ($V_2S_3O_2$). Vanadium resembles arsenic, phosphorus, and nitrogen, both in the chemical structure of its compounds and in their behavior toward reagents.

Estimation.* *A. Gravimetric.* Vanadium is usually weighed as the pentoxide, (V_2O_5), obtained (1) by precipitation of lead or barium vanadate, treatment with sulphuric acid, filtration, evaporation of the filtrate, and ignition; (2) by precipitation of mercury vanadate and ignition, the pentoxide being left; or (3) by precipitation of the ammonium salt by ammonium chloride and ignition (Berzelius, Pogg. Annal. XXII, 54; Gibbs, Amer. Chem. Jour. V, 371; Gooch and Gilbert, Amer. Jour. Sci. [4] XIV, 205).

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* See Die analytische Chemie des Vanadins, V. von Klecki, pub. by Leopold Voss, Hamburg, 1894.

B. Volumetric. Vanadium may be estimated volumetrically (1) by reduction from the condition of the pentoxide to that of the tetroxide by sulphur dioxide, and reoxidation by permanganate (Hillebrand, Jour. Amer. Chem. Soc. XX, 461); (2) by effecting the reduction by boiling with hydrochloric acid or with potassium bromide or iodide in acid solution, according to the typical equation $V_2O_5 + 2HCl = V_2O_4 + H_2O + Cl_2$. The chlorine, bromine, or iodine may be distilled, and determined by suitable means in the distillate (Holverscheit, Dissertation, Berlin, 1890; Friedheim, Ber. Dtsch. chem. Ges. XXVIII, 2067; Gibbs, Proc. Amer. Acad. x, 250; Gooch and Stookey, Amer. Jour. Sci. [4] XIV, 369; Curtis, Amer. Jour. Sci. [4] XVI), or the residue after boiling may be rendered alkaline by potassium bicarbonate, and reoxidation effected by standard iodine solution (Browning, Amer. Jour. Sci. [4] II, 185); (3) or the reduction may be accomplished by boiling with tartaric, oxalic, or citric acid, and reoxidation effected as outlined above (Browning, Zeitsch. anorg. Chem. VII, 158, and Amer. Jour. Sci. [4] II, 355).

Separation. Vanadium may be separated from the majority of the metallic bases (1) by fusion of material containing it with sodium carbonate and potassium nitrate and extraction with water, vanadium dissolving as sodium vanadate; or (2) by treatment of a solution containing a vanadate with ammonium sulphide in excess, vanadium remaining in solution as a sulpho salt.

From arsenic vanadium may be separated (1) by treatment with hydrogen sulphide, after reduction by means of sulphur dioxide, the arsenic being precipitated as the sulphide As_2S_3; (2) by heating the sulphides of vanadium and arsenic in a current of hydrochloric-acid gas at 150° C., the arsenic forming a volatile compound (Field and Smith, Jour. Amer. Chem. Soc. XVIII, 1051).

From phosphorus vanadium may be separated by re-

duction of vanadic acid by means of sulphur dioxide, and precipitation of the phosphorus as phosphomolybdate.

From molybdenum the separation may be accomplished by the action of hydrogen sulphide upon a solution of vanadic and molybdic acids under pressure,—molybdenum sulphide being precipitated,—or by the action of ammonium chloride in excess upon a solution containing an alkali vanadate and molybdate,—ammonium metavanadate being precipitated (Gibbs, Amer. Chem. Jour. v, 371).

From tungsten vanadium may be separated by the ammonium chloride method (*vid.* Separation from molybdenum, above) (Gibbs, Amer. Chem. Jour. v, 379).

EXPERIMENTAL WORK ON VANADIUM.

Experiment 82. *Extraction of vanadic pentoxide from vanadinite*, $((PbCl)Pb_4(VO_4)_3)$. Treat a few grams of the finely powdered mineral with nitric acid, heat until nothing further dissolves, dilute and filter. Remove the lead from the filtrate by hydrogen sulphide, filter again, and evaporate the filtrate to dryness, adding a little nitric acid after the hydrogen sulphide has boiled out, to insure the oxidation of the vanadium. Ignite the residue.

Experiment 83. *Formation of insoluble vanadates of lead, silver, and barium*, ($\overset{II}{R}_3(VO_4)_2$, *ortho; or* $\overset{II}{R}(VO_3)_2$, *meta*).

(*a*) To a solution of an alkali vanadate (ortho or meta) add a solution of lead acetate.

(*b*) Repeat the experiment, substituting silver nitrate for lead acetate. Note the flocky character of the precipitate when shaken.

(*c*) Use barium chloride as the precipitant.

(*d*) Try the action of nitric and acetic acids upon these salts.

Experiment 84. *Formation of vanadium pentoxide*, (V_2O_5), *from ammonium vanadate.* Evaporate a solution of ammonium vanadate to dryness and ignite. Note the crystals of the pentoxide.

Experiment 85. *Precipitation of vanadium oxysulphide*, ($V_2S_3O_2$). (*a*) To a solution of an alkali vanadate add ammonium sulphide. Note the darkening in color ($(NH_4)_3S_3VO$?). Acidify the solution with hydrochloric acid. Note the precipitation of the oxysulphide.

(*b*) Note that hydrogen sulphide in an acid solution precipitates sulphur and leaves a blue solution (V_2O_4).

Experiment 86. *Reduction of vanadic acid*, (V_2O_5). (*a*) To a solution of an alkali vanadate add a crystal of tartaric acid and boil. Note the yellow-red color of the vanadic acid when the tartaric acid is first added, and the change to blue (V_2O_4) produced on boiling.

(*b*) Neutralize the blue solution obtained in (*a*) with sodium or potassium bicarbonate, and add a solution of iodine in potassium iodide until, after the liquid has stood for a few moments, the color of the iodine remains. Bleach the excess of iodine with an alkaline solution of arsenious oxide. Note that the blue color has disappeared and the vanadium is in the condition of the pentoxide (V_2O_5).

(*c*) Try the action of other reducing agents upon vanadic acid, e.g. oxalic acid, hydrochloric acid, stannous chloride, zinc and hydrochloric acid, etc. Note that the zinc and hydrochloric acid carry the reduction below the tetroxide condition (V_2O_4).

Experiment 87. *Delicate tests for vanadium.* (*a*) Acidify a solution of an alkali vanadate and add hydrogen dioxide. Note the red color (Maillard).

(*b*) Bring a few drops of the vanadium solution into contact with a drop of strong sulphuric acid to which a crystal of strychnine sulphate has been added Note the color, changing from violet to rose.

Experiment 88. *Borax-bead tests for vanadium.* Fuse a little ammonium vanadate into a borax bead and test the action of the reducing and oxidizing flames upon it.

MOLYBDENUM, Mo, 96.

Discovery. The name Molybdena, derived from μόλυβδος, *lead*, was originally applied to a variety of substances containing lead. Later the term was used to designate only graphite and a mineral sulphide of molybdenum which is very similar in appearance to graphite, and which was confused with it. In 1778 Scheele, in his treatise on molybdena (Kong. Vet. Acad. Handl. (1778), 247), showed that it differs from plumbago, or graphite, in that on being heated with nitric acid it yields a peculiar white earth, which he proved to be an acid-forming oxide. This he called "acidum molybdenæ," and he supposed the mineral to be a compound of this oxide with sulphur. In 1790 Hjelm (ibid. (1790), 50; Ann. de Chim. IV, 17) isolated the element.

Occurrence. Molybdenum occurs in combination in minerals which are somewhat widely diffused, though found in small amounts:

	Contains Mo
Molybdite, MoO_3	66–67%
Molybdenite, MoS_2	60%
Powellite, $Ca(Mo,W)O_4$	58–59%*
Wulfenite, $PbMoO_4$	37–40%*
Belonesite, $MgMoO_4$?	78–79%*
Scheelite, $CaWO_4$	traces– 8%*

Extraction. Molybdenum salts are usually obtained from molybdenite, the most abundant ore, though some-

* MoO_3.

times from other minerals. The following processes will illustrate the methods employed.

(1) *From molybdenite.* The mineral is roasted until sulphur dioxide is no longer given off and the residue is yellow when hot and white when cold. This residue is dissolved in dilute ammonium hydroxide, and the solution is evaporated to crystallization. Heat drives off the ammonia from the crystals and leaves the trioxide of molybdenum.

(2) *From molybdenite.* The mineral is treated with nitric acid (*vid.* Experiment 89).

(3) *From wulfenite.* The mineral is fused with potassium polysulphide. Upon extraction with water the lead remains insoluble, as the sulphide, and the molybdenum goes into solution as the sulpho salt. The filtrate is acidified with sulphuric acid, and the sulphide of molybdenum is precipitated (Wittstein).

The Element. *A. Preparation.* Elementary molybdenum may be prepared (1) by passing dry hydrogen over either the trioxide or the ammonium salt at red heat, and (2) by reducing the chlorides with hydrogen.

B. Properties. Molybdenum is a gray metallic powder, which is unchanged in the air at ordinary temperatures, but which, when heated, passes gradually into the trioxide. It is insoluble in hydrochloric, hydrofluoric, and dilute sulphuric acids, but soluble in nitric and concentrated sulphuric acids, in aqua regia, in chlorine water, and in melted potassium hydroxide, and potassium nitrate. Its specific gravity is 8.6.

Compounds. *A. Typical forms.* The following are typical compounds of molybdenum:

Oxides.......	MoO	Mo_2O_3	MoO_2	Mo_5O_{12}	Mo_3O_8		MoO_3
Chlorides.....	$MoCl_2$	$MoCl_3$	$MoCl_4$			$MoCl_5$	
Oxychlorides.							$MoOCl_4$
							MoO_2Cl_2
Bromides....	$MoBr_2$	$MoBr_3$	$MoBr_4$				

Oxybromide..			MoO_2Br_2
Oxyiodide....		MoO_2I	
Oxyfluorides.		$MoOF_3 \cdot 2KF + H_2O$	$MoO_2F_2 \cdot KF + H_2O$
Sulphides....	MoS_2		MoS_3; MoS_4
Sulpho salt...			$\overset{I}{R}_2MoS_4$

Molybdates, many salts of the type $\overset{I}{R}_2MoO_4$, as K_2MoO_4; $CaMoO_4$; $ZnMoO_4$; Ag_2MoO_4; etc.

Molybdenum trioxide combines with phosphoric pentoxide in the following proportions: $P_2O_5 : MoO_3 :: 1:24$, $1:22$, $1:20$, $1:18$, $1:16$, $1:15$, $1:5$, as $2K_2HPO_4 \cdot 24MoO_3 + 3H_2O$; $2(NH_4)_3PO_4 \cdot 16MoO_3 + 14H_2O$; etc. It combines with arsenic pentoxide as follows: $As_2O_5 : MoO_3 :: 1:20$, $1:18$, $1:16$, $1:6$, $1:2$, as $As_2O_5 \cdot 20MoO_3 + 27H_2O$; $10NH_3 \cdot As_2O_5 \cdot 16MoO_3 + 14H_2O$; etc.

B. Characteristics. The molybdenum compounds are known in various conditions of oxidation (*vid.* Typical Forms), of which the highest, (MoO_3), is the most stable and comprises the largest number of salts. The trioxide is white to pale yellow, and dissolves in potassium, sodium, and ammonium hydroxides, forming the molybdates. When strong reducing agents, such as zinc and hydrochloric acid, act upon acid solutions of molybdates, the reduction is said to go as far as the oxide Mo_5O_7, the solution passing through the colors of the various oxides, violet, blue, and black. The oxide Mo_5O_7, however, is very sensitive to oxidation, for it is changed in the air to the sesquioxide (Mo_2O_3) as soon as the reducing action has ceased. Acid solutions of the lower oxides give, on treatment with the alkali hydroxides, the corresponding hydroxides of molybdenum, $Mo_2O_3 \cdot 3H_2O$; $MoO_2 \cdot xH_2O$; etc. The sulphide (MoS_3) is obtained by treating a molybdate with ammonium sulphide and acidifying. Its color is reddish brown.

Estimation. *A. Gravimetric.* Molybdenum is generally

weighed as the oxide (MoO_3), obtained (1) by ignition of ammonium molybdate; (2) by precipitation of mercury molybdate and ignition; or (3) by precipitation of the sulphide and conversion into the oxide by treatment with nitric acid.

B. Volumetric. Soluble molybdates may be reduced in acid solution by boiling with potassium iodide, and the iodine thus liberated may be passed into potassium iodide and estimated by standard thiosulphate, the amount of molybdenum present being calculated from the equation $2MoO_3 + 2HI = Mo_2O_5 + I_2 + H_2O$; or, after the iodine has been removed by boiling, the residual solution may be rendered alkaline by potassium bicarbonate and reoxidized by standard iodine solution or potassium permanganate (Mauro and Danesi, Zeitsch. anal. Chem. XX, 507; Friedheim and Euler, Ber. Dtsch. chem. Ges. XXVIII, 2066; Gooch and Fairbanks, Amer. Jour. Sci. [4] II, 156; Gooch and Pulman, Amer. Jour. Sci. [4] XII, 449).

Separation. The general methods for the separation of molybdenum from the metals and alkali earths are the same as those described under Vanadium.

From arsenic and phosphorus, when present as arsenic and phosphoric acids, molybdenum may be separated by magnesium chloride mixture in ammoniacal solution, ammonium-magnesium arseniate and phosphate being precipitated (Gibbs, Amer. Chem. Jour. VII, 317; Gooch, Amer. Chem. Jour. I, 412).

For the separation from vanadium, *vid.* Vanadium.

From tungsten molybdenum may be separated (1) by the action of warm sulphuric acid of specific gravity 1.37 upon the oxides (MoO_3 and WO_3), molybdic acid dissolving (Ruegenberg and Smith, Jour. Amer. Chem. Soc. XXII, 772); (2) by heating the oxides with hydrochloric-acid gas at 250°–270° C., the molybdenum compound ($MoO_3 \cdot 2HCl$) being volatilized (Pechard, Compt. rend.

CXIV, 173; Debray, ibid. XLVI, 1101); (3) by precipitation of the sulphide of molybdenum by means of hydrogen sulphide in the presence of tartaric acid (Rose, Handbuch der anal. Chemie (sechste Auflage, 1871), 358).

EXPERIMENTAL WORK ON MOLYBDENUM.

Experiment 89. *Extraction of molybdenum salts from molybdenite*, (MoS_2). Heat 5 grm. of the finely powdered mineral with nitric acid until the dark color has disappeared. Evaporate to dryness, wash the residue in warm dilute nitric acid, then in water, and dissolve it in ammonium hydroxide. Filter, and evaporate the filtrate to a small volume. Ammonium molybdate crystallizes out, which may be converted into the trioxide by careful ignition.

Experiment 90. *Precipitation of the sulphides of molybdenum*, (MoS_2; MoS_3). (*a*) Through a solution of ammonium molybdate acidified with hydrochloric acid pass hydrogen sulphide. Note the gradual change of color of the solution, from red-brown to blue, and the partial precipitation of the sulphide MoS_2.

(*b*) To a solution of ammonium molybdate add ammonium sulphide, or pass hydrogen sulphide through an alkaline solution of a molybdate. Note the yellow-brown color ($(NH_4)_2MoS_4$, typical). Acidify the solution and note the brown precipitate (MoS_3).

Experiment 91. *Precipitation of ammonium phosphomolybdate* ($3(NH_4)_2O \cdot P_2O_5 \cdot 24(MoO_3) + 2H_2O$). To a solution of ammonium molybdate acidified with nitric acid add a drop of a solution of sodium phosphate, and warm gently. Note the yellow precipitate.

Experiment 92. *Precipitation of the molybdates of silver, lead, and barium*, (Ag_2MoO_4, $PbMoO_4$, and $BaMoO_4$, *typical*). To separate solutions of ammonium molybdate,

neutral or faintly acid with acetic acid, add solutions of silver nitrate, lead acetate, and barium chloride respectively. Note the solvent action of nitric acid upon the precipitates.

Experiment 93. *Reduction of molybdic acid,* (MoO_3). (*a*) Put a piece of metallic zinc into a solution of ammonium molybdate and add hydrochloric acid until the action starts. Note the change in color of the solution as the reduction proceeds (reddish yellow, violet, bluish, black). To a few drops of the solution after reduction add potassium or sodium hydroxide. Note the dark-brown precipitate of the lower hydroxides of molybdenum ($Mo_2(OH)_6$, etc.) mixed with the hydroxide of zinc.

(*b*) Try the reducing action of stannous chloride upon a molybdate in solution.

(*c*) To a dilute solution of a molybdate which has been treated with zinc and hydrochloric acid, add some potassium sulphocyanide in solution. Note the red color. Try the effect of adding ether and shaking.

Experiment 94. *Preparation of elementary molybdenum from ammonium molybdate.* Heat a few grams of finely powdered ammonium molybdate until no further test for ammonia is obtained when a piece of moistened red litmus paper is held over the substance. Remove the molybdic trioxide thus obtained to a Rose crucible and heat for some time in a current of hydrogen. Note the gray powder.

TUNGSTEN, W, 184.

Discovery. The minerals scheelite, formerly called tungsten (i.e. "heavy stone"), and wolframite have long been known, but until about the middle of the eighteenth century they were regarded as tin ores. In 1781 Scheele (Kong. Vet. Acad. Handl. (1781), 89) demonstrated that scheelite contained a peculiar acid which he named Tung-

stic acid. Two years later the brothers D'Elhujar showed the presence of the same acid in wolframite.

Occurrence. Tungsten is found combined in minerals which are often associated with tin ores:

	Contains WO_3.
Wolframite, $(Fe,Mn)WO_4$.	74–78%
Scheelite, $CaWO_4$.	71–80%
Hübnerite, $MnWO_4$.	73–77%
Cuprotungstite, $CuWO_4$.	56–57%
Cuproscheelite, $(Ca,Cu)WO_4$	76–80%
Powellite, $Ca(Mo,W)O_4$	10–11%
Stolzite, $PbWO_4$	51 *circa*
Raspite, $PbWO_4$	49 "
Reinite, $FeWO_4$.	75–76%
Tungstite, WO_3.	100 *circa*

Extraction. Tungstic acid is usually extracted from wolframite. Either of the processes here indicated may be followed:

(1) 5 parts of the mineral are fused with 8.5 parts of dry sodium carbonate and 1.5 parts of sodium nitrate. On treatment of the fused mass with water, sodium tungstate is dissolved, and after filtration tungstic acid is precipitated by hydrochloric acid.

(2) The mineral is decomposed by hydrochloric acid (*vid.* Experiment 95).

The Element. *A. Preparation.* Elementary tungsten may be obtained (1) by heating the acid in the presence of hydrogen; (2) by heating the chloride (WCl_6) in the presence of hydrogen; (3) by heating the acid with carbon; (4) by heating the nitride.

B. Properties. Tungsten is a very hard powder ranging in color from gray to brownish black, resembling sometimes tin, sometimes iron. Although unchanged in the air

at ordinary temperatures, when heated in finely divided condition it ignites and burns to the oxide (WO_3). It dissolves when heated with sulphuric, hydrochloric, and nitric acids. It is attacked by dry chlorine at high temperatures; also by concentrated boiling potassium hydroxide, with the formation of potassium tungstate. The specific gravity of tungsten is from 16.5 to 19.1.

Compounds. *A. Typical forms.* The following compounds of tungsten may be considered typical:

Oxides*.........		WO_2		WO_3
Chlorides.........	WCl_2	WCl_4	WCl_5	WCl_6
Oxychlorides.....				$WOCl_4$
				WO_2Cl_2
Bromides	WBr_2		WBr_5	
Oxybromides.....				$WOBr_4$
				WO_2Br_2
Iodide...........	WI_2			
Double fluorides ..			$KF \cdot WO_2F + H_2O$	$ZnF_2 \cdot WO_2F_2 + 10H_2O$; etc.
Sulphides........		WS_2		WS_3
Sulpho salts......				R_2WS_4
				$R_2WS_2O_2$
				R_2WSO_3
Tungstates, many salts of the types,				R_2WO_4 (normal)
				$R_2W_4O_{13}$ (meta)
				$R_6W_7O_{24}$ (para)

Tungstic trioxide (acid) combines with phosphoric pentoxide, arsenic pentoxide, and silicon dioxide in the following proportions:

$$P_2O_5 : WO_3 :: 1:22,\ 1:21,\ 1:20,\ 1:16,\ 1:12,\ 1:7.$$
$$As_2O_5 : WO_3 :: 1:16,\ 1:6,\ 1:3.$$
$$SiO_2 : WO_3 :: 1:12,\ 1:10.$$

B. Characteristics. The compounds of tungsten are very similar to those of molybdenum, and are known

* Some authorities give three oxides between the dioxide and the trioxide, viz., W_2O_5, W_3O_8, and W_4O_{11}.

in several conditions of oxidation (*vid.* Typical Forms), of which the highest is the most stable. The trioxide, (WO_3), united with the bases, forms the largest number of salts, the tungstates. When acted upon by reducing agents, tungstic acid or trioxide may be reduced to the dioxide, (WO_2), the solution becoming blue, then brown. When the solution of a tungstate is acidified, tungstic acid is precipitated. Tungstic sulphide, (WS_3), is obtained under the same conditions as molybdenum sulphide, and is brown. It dissolves in ammonium sulphide, forming a sulpho salt.

Estimation. Tungsten is ordinarily weighed as the oxide (WO_3), obtained (1) by igniting ammonium tungstate; (2) by decomposing the alkali tungstates with nitric acid, evaporating to dryness, and extracting with water,—tungstic acid remaining undissolved; (3) by precipitating mercury tungstate and driving off the mercury by means of heat, leaving the acid or oxide; (4) by boiling fused lead tungstate with strong hydrochloric acid,—tungstic acid being precipitated (Brearley, Chem. News LXXIX, 64).

Separation. Tungsten may be separated from the metallic bases and many other elements by the following process: fusion with an alkali carbonate, extraction of the alkali tungstate with water, acidification with nitric acid, evaporation to dryness, and extraction with water,—tungstic acid remaining undissolved.

For the separation of tungsten from molybdenum and vanadium, see those elements. From arsenic and phosphorus tungsten is separated by magnesium mixture (Gooch, Amer. Chem. Jour. I, 412; Gibbs, Amer. Chem. Jour. VII, 337).

From tin the separation may be accomplished (1) by ignition with ammonium chloride, tin chloride being volatilized (Rammelsberg); (2) by fusion with potassium cyanide, the tin being reduced to the metal and the tungsten being converted into a soluble tungstate (Talbot).

EXPERIMENTAL WORK ON TUNGSTEN.

Experiment 95. *Extraction of tungstic acid from wolframite* ($(Fe,Mn)WO_4$). Treat 5 grm. of the finely powdered mineral with about 10 $cm.^3$ of a mixture of equal parts of hydrochloric acid and water, and boil as long as any action seems to take place. Decant the solution, add to the residue about 10 $cm.^3$ of a mixture of nitric and hydrochloric acids (aqua regia), and warm. Add more acid if necessary, and continue this treatment until the residue is yellow, then filter and wash. Warm the yellow mass with ammonium hydroxide as long as any solvent action is observed, and filter. Evaporate the filtrate to dryness and ignite the ammonium tungstate to obtain tungstic acid.

Experiment 96. *Formation of sodium tungstate*, (Na_2WO_4, *typical*). Dissolve a little tungstic acid in a solution of sodium carbonate.

Experiment 97. *Precipitation of tungstic sulphide*, (WS_3), *and formation of the sulpho salt* ($(NH_4)_2WS_4$). (*a*) To a solution of sodium or ammonium tungstate add ammonium sulphide, and acidify with hydrochloric acid.

(*b*) Try the action of hydrogen sulphide upon a soluble tungstate.

(*c*) Try the action of ammonium sulphide upon tungstic sulphide.

Experiment 98. *Precipitation of tungstic acid*, (WO_3). Acidify a concentrated solution of a tungstate with hydrochloric or nitric acid and boil.

Experiment 99. *Precipitation of barium, lead, and silver tungstates*, ($\overset{I}{R}_2WO_4$, *typical*). To separate portions of a solution of sodium tungstate acidified with acetic acid add solutions of barium, lead, and silver salts respectively.

Experiment 100. *Reduction of tungstic acid*. (*a*) To a solution of a tungstate (e.g. sodium tungstate) add a

solution of stannous chloride. Acidify with hydrochloric acid and warm gently.

Experiment 101. *Salt of phosphorus bead tests.* Make a bead of microcosmic salt, and heat it in the oxidizing and reducing flames with a small particle of tungstic acid. Try the effect of a small amount of ferrous sulphate upon the bead heated in the reducing flame.

URANIUM, U, 238.5.

Discovery. Klaproth, in the year 1789, discovered that the mineral pitch-blende, supposed to be an ore of zinc, iron, or tungsten, contained a "half-metallic substance" differing in its reactions from all three (Crell Annal. (1789) II, 387). This he named Uranium in honor of Herschel's discovery of the planet Uranus in 1781. The body that Klaproth obtained was really an oxide of uranium, as Péligot showed in 1842, when he succeeded in isolating the metal (Ann. de Chim. (1842) V, 5).

Occurrence. Uranium is found combined in a few minerals, most of them rare. Pitch-blende is the most abundant source.

Uraninite (pitch-blende), $UO_3 \cdot UO_2 \cdot PbO \cdot N$, etc.,	contains	75–85% $(UO_2 + UO_3)$
Gummite, $(Pb,Ca)U_3SiO_{12} \cdot 6H_2O$?,	"	61–75% UO_3
Thorogummite, $UO_3 \cdot 3ThO_2 \cdot 3SiO_2 \cdot 6H_2O$,	"	22–23% "
Mackintoshite, $UO_2 \cdot 3ThO_2 \cdot 3SiO_2 \cdot 3H_2O$,	"	21–22% UO_2
Uranophane, $CaO \cdot 2UO_3 \cdot 2SiO_2 \cdot 6H_2O$,	"	53–67% UO_3
Uranosphaerite, $(BiO)_2U_2O_7 \cdot 3H_2O$,	"	50–51% "
Walpurgite, $Bi_{10}(UO_2)_3(OH)_{24}(AsO_4)_4$,	"	20–21% "
Carnotite, $K_2O \cdot 2U_2O_3 \cdot V_2O_5 \cdot 3H_2O$,	"	62–65% U_2O_3
Torbernite, $Cu(UO_2)_2P_2O_8 \cdot 8H_2O$,	"	57–62% UO_3
Zeunerite, $Cu(UO_2)_2As_2O_8 \cdot 8H_2O$,	"	55–56% "
Autunite, $Ca(UO_2)_2P_2O_8 \cdot 8H_2O$,	"	55–62% "
Uranospinite, $Ca(UO_2)_2As_2O_8 \cdot 8H_2O$,	"	59–60% "
Uranocircite, $Ba(UO_2)_2P_2O_8 \cdot 8H_2O$,	"	56–57% "
Johannite, sulphate, formula doubtful,	"	67–68% "
Uranopilite, $CaO \cdot 8UO_3 \cdot 2SO_3 \cdot 25H_2O$,	"	77–78% "
Thorite, $ThSiO_4$,	"	1–10% "

Phosphuranylite, $(UO_2)_3P_2O_8 \cdot 6H_2O$,	contains..	72–77% UO_3
Trögerite, $(UO_2)_3As_2O_8 \cdot 12H_2O$,	" ..	63–64% "
Uranothallite, $2CaCO_3 \cdot U(CO_3)_2 \cdot 10H_2O$,	" ..	35–37% UO_2
Liebigite, $CaCO_3 \cdot (UO_2)CO_3 \cdot 20H_2O$,	" ..	36–38% UO_3
Voglite, complex carbonate,	" ..	37% UO_2
Hatchettolite, $R(Nb,Ta)_2O_6 \cdot H_2O$,	" ..	15–16% UO_3
Fergusonite, $\overset{III}{R}(Nb,Ta)O_4$,	" ..	0– 8% UO_2
Sipylite, complex niobate,	" ..	3– 4% "
Samarskite, $\overset{II}{R}_3\overset{III}{R}_2(Nb,Ta)_6O_{21}$,	" ..	10–13% UO_3
Ånnerödite, complex,	" ..	16–17% UO_2
Hielmite, complex,	" ..	0– 5% "
Euxenite, $\overset{III}{R}(NbO_3)_3 \cdot \overset{III}{R}_2(TiO_3)_3 \cdot \frac{3}{2}H_2O$,	" ..	5–12% "
Polycrase, $\overset{III}{R}(NbO_3)_3 \cdot 2\overset{III}{R}(TiO_3)_3 \cdot 3H_2O$,	" ..	1–19% "

Extraction. Uranium salts may be extracted from pitchblende as follows:

(1) The mineral is decomposed with nitric acid, the acid solution is evaporated to dryness, and the mass is extracted with water. The residue, which consists largely of lead sulphate, iron arseniate, and iron oxide, is filtered off, and on evaporation of the solution impure nitrate of uranium crystallizes out, which may be purified by recrystallization (Péligot).

(2) The mineral is decomposed by aqua regia (*vid.* Experiment 102).

The Element. *A. Preparation.* Metallic uranium may be obtained (1) by heating a mixture of the chloride UCl_4 with sodium and potassium chloride in a porcelain crucible surrounded by powdered carbon contained in another crucible (Péligot); (2) by heating a mixture of uranium chloride, sodium chloride, and metallic sodium in a closed iron crucible.

B. Properties. Uranium is a somewhat malleable white metal with much the appearance of nickel. Heated in air or oxygen to a temperature of 150°–170° C. it burns

to the oxide; at ordinary temperatures the oxidation takes place slowly. Uranium dissolves slowly in cold dilute sulphuric acid, and more rapidly upon the application of heat. It is soluble in nitric and hydrochloric acids. It is attacked by chlorine at 150° C. and by bromine at 240° C. The caustic alkalies have no apparent action upon the element. The specific gravity of uranium is 18.6.

Compounds. *A. Typical forms.* The following are typical compounds of uranium:

Oxides *........		UO_2	$U_3O_8(UO_2+2UO_3)$	UO_3
Carbonates......				$UO_2CO_3 \cdot 2K_2CO_3$
				$UO_2CO_3 \cdot 2(NH_4)_2CO_3$
Chlorides.........	UCl_3	UCl_4	UCl_5	UO_2Cl_2
Bromides........	UBr_3	UBr_4	UBr_5	UO_2Br_2
Iodate..........				$UO_2(IO_3)_2$
Fluorides........		UF_4		UO_2F_2
				$UO_2F_2 \cdot NaF$, etc.
Sulphides........US	U_2S_3	US_2		UOS_2
				UO_2S
Sulphates........		$U(SO_4)_2+4H_2O$		$UO_2SO_4+3\frac{1}{2}H_2O$
Nitrate..........				$UO_2(NO_3)_2+6H_2O$
Nitride..........		U_3N_4		
Ferrocyanides....		$UFe(CN)_6$		$(UO_2)_3K_2(FeC_6N_6)_2$
Phosphates, ortho.		$UOHPO_4$		$(UO_2)_5H_2(PO_4)_4$
pyro..		$(UO)_2P_2O_7$		$(UO_2)_2P_2O_7$
meta..		$UO(PO_3)_2$		$UO_2(PO_3)_2$
Arseniate........				$UO_2HAsO_4+4H_2O$

Uranates, of types R_2UO_4, $R_2U_2O_7$, and R_4UO_5.

B. Characteristics. Uranium differs from vanadium, molybdenum, and tungsten in manifesting less marked acidic qualities. The chief classes of salts are the uranyl, in which uranium shows its highest degree of oxidation, corresponding to the oxide UO_3 (e.g. UO_2Cl_2), and the uranous, of which the oxide UO_2 is the type (e.g. UCl_4). The uranyl salts are the more stable and better known. They may be reduced by zinc and hydrochloric acid to

* Other oxides less well known than those given above are of the following forms: UO, U_2O_3, U_3O_4, and UO_4.

the lower condition. The uranous salts are easily oxidized to the higher form. The uranyl salts are, in general, yellow, the uranous greenish. The two conditions of oxidation may be further distinguished by the following reactions: the precipitate resulting from the action of ammonium sulphide upon uranyl salts is reddish brown,—upon uranous salts, light green; the precipitate resulting from the action of potassium ferrocyanide upon uranyl salts is blood-red,—upon uranous salts yellowish green. Uranates of the types $\overset{I}{R}_2UO_4$ and $\overset{I}{R}_2U_2O_7$ are formed by the combination of the oxide UO_3 with the strong bases.

Estimation.* *A. Gravimetric.* Uranium may be weighed (1) as urano-uranic oxide (U_3O_8), obtained by precipitation of ammonium uranate by means of ammonia, and ignition in air or oxygen; (2) as urano-uranic oxide, precipitated electrolytically by a current of 0.18 ampere and 3 volts at a temperature of 70° C. (Smith and Wallace, Jour. Amer. Chem. Soc. XX, 279; Smith and Kollock, ibid. XXIII, 607); (3) as uranous oxide (UO_2), obtained by ignition of urano-uranic oxide in a current of hydrogen; (4) as the pyrophosphate ($(UO_2)_2P_2O_7$), obtained by precipitation by means of ammonium phosphate in the presence of ammonium acetate, and ignition.

B. Volumetric. Uranium may be estimated volumetrically by reduction from the higher (UO_3) to the lower (UO_2) condition of oxidation by means of zinc and sulphuric acid, and oxidation with permanganate, according to the following formulæ (Pulman, Amer. Jour. Sci. [4] XVI):

(1) $UO_2SO_4 + Zn + 2H_2SO_4 = ZnSO_4 + U(SO_4)_2 + 2H_2O$;

(2) $2KMnO_4 + 5U(SO_4)_2 + 2H_2O =$
$$2KHSO_4 + 2MnSO_4 + H_2SO_4 + 5UO_2SO_4.$$

Separation.* From the metals which precipitate sulphides with hydrogen sulphide in acid solution, uranium

* *Vid.* Kern, Jour. Amer. Chem. Soc. XXIII, 685.

may be separated by hydrogen sulphide. From iron, nickel, and other members of its own group it may be separated by ammonium sulphide in the presence of an excess of sodium or ammonium carbonate, the uranium salt remaining in solution. From the alkalies and alkali earths the separation may be accomplished by means of ammonium sulphide in the presence of ammonium chloride, uranium oxysulphide being precipitated.

EXPERIMENTAL WORK ON URANIUM.

Experiment 102. *Extraction of uranium salts from pitch-blende.* Warm 5 grm. of pulverized pitch-blende with aqua regia until the decomposition is complete, and remove the excess of acid by evaporation. Extract with water and boil the solution a few minutes with sulphurous acid to reduce the arsenic acid. When the liquid is at about 60° C., pass hydrogen sulphide through to the complete precipitation of arsenic, copper, lead, bismuth, and tin. Filter, oxidize the filtrate with nitric acid, and precipitate with ammonium hydroxide. Treat the precipitate with hot concentrated ammonium carbonate, filter, and allow the filtrate to cool. The double carbonate of uranium and ammonium will separate. A further precipitate, of crude ammonium uranate, may be obtained by boiling the mother-liquor.

Experiment 103. *Precipitation of sodium, potassium, or ammonium uranate,* ($\overset{\text{I}}{R}_2U_2O_7$, *typical*). To a solution of a uranyl salt add sodium, potassium, or ammonium hydroxide. Note the yellow color of the precipitate and the insolubility in excess of the reagent. Repeat the experiment with tartaric acid present in the solution.

Experiment 104. *Formation of the soluble double carbonates of uranium with sodium or potassium, and uranium*

Montanite, $Bi_2(OH)_4TeO_6$?,	contains..	24–28% TeO_3
Emmonsite, formula doubtful,	" ..	59–60% Te
Durdenite, $Fe_2(TeO_3)_3 \cdot 4H_2O$,	" ..	47–64% TeO_2
Tellurium (native), Te,	" ..	93–97% Te
Selen-tellurium, 3Te2Se,	" ..	70–71% "

Extraction. Tellurium may be extracted by the following methods:

(1) *From tellurium bismuth (tetradymite).* The mineral is mixed with its own weight of sodium carbonate, and oil is added until the mass has the consistency of thick paste. This is heated strongly in a well-closed crucible and then extracted with water. The extract, containing sodium sulphide and sodium telluride, (Na_2Te), is separated by filtration from the insoluble matter and left exposed to the air. The tellurium separates as a gray powder. It may be purified by distillation (Berzelius).

(2) *From sylvanite or nagyagite.* The mineral is treated with hydrochloric acid, which dissolves the antimony, arsenic, etc. The residue is dissolved in aqua regia, the excess of acid is removed by evaporation, and the gold is precipitated by ferrous sulphate. After the removal of the gold by filtration the tellurium is precipitated by sulphur dioxide (Von Schrötter).

(3) *From flue-dust containing tellurium.* The material is treated with strong commercial hydrochloric acid (*vid.* Experiment 109).

The Element. *A. Preparation.* Elementary tellurium may be obtained (1) by the action of reducing agents, as sulphurous acid or stannous chloride, upon the salts of tellurium; and (2) by the action of air upon soluble tellurides.

B. Properties. Tellurium is generally considered a non-metal, though Berzelius classed it with the metals. It is known in two conditions: (1) the crystalline, in which the element has a luster like silver, and (2) the amorphous. It

is unchanged in the air at ordinary temperatures, but when heated in air or oxygen it burns with a green flame, forming the dioxide (TeO_2). It is not attacked by hydrochloric acid, but is acted upon slowly by concentrated sulphuric acid, with evolution of sulphur dioxide. It is oxidized by nitric acid and aqua regia to tellurous acid, (H_2TeO_3), and is dissolved in hot caustic potash, forming the telluride and tellurite (K_2Te; K_2TeO_3). It combines with metals to form tellurides. Like selenium and sulphur, it is a poor conductor of heat and electricity. Its specific gravity is from 6.1 to 6.3.

Compounds. *A. Typical forms.* The following are typical compounds of tellurium:

Oxides	TeO	TeO_2	TeO_3
Chlorides	$TeCl_2$	$TeCl_4$	
Oxychloride		$TeOCl_2$	
Bromides	$TeBr_2$	$TeBr_4$	
Oxybromide		$TeOBr_2$	
Iodides	TeI_2	TeI_4	
Fluoride		TeF_4	
Double fluoride		$TeF_4 \cdot KF$	
Sulphite	$TeSO_3$		
Sulphate		$2TeO_2 \cdot SO_3$	
Sulphides (or sulpho salts)		$TeS_2 \cdot 3K_2S$ $TeS_2 \cdot Bi_2S_3$, etc.	
Tellurides	H_2Te As_2Te_3 K_2Te, etc.		
Acids (tellurous and telluric)		H_2TeO_3	H_2TeO_4*
Salts (tellurites and tellurates)		R_2TeO_3	R_2TeO_4

B. Characteristics. The compounds of tellurium closely resemble in general structure those of sulphur, and, as will appear later, those of selenium. Hydrogen telluride, (H_2Te),

* Gutbier favors the formula H_6TeO_6.

like hydrogen sulphide, is a gaseous substance, and it precipitates metallic tellurides, ($\overset{I}{R}_2Te$), similar to the sulphides. Two oxides, tellurous, (TeO_2), and telluric, (TeO_3), are well known,* but, unlike the corresponding oxides of sulphur, they are very sparingly soluble in water. The acids, (H_2TeO_3; H_2TeO_4), may be formed by acidifying solutions of the alkali salts (e.g. Na_2TeO_3 or Na_2TeO_2) which have been formed by the action of the alkali hydroxides upon the oxides (TeO_2; TeO_3). Many tellurites and tellurates, (R_2TeO_3; R_2TeO_4), may be formed by treating the alkali tellurites or tellurates with soluble salts of the various bases. Two chlorides are known, ($TeCl_2$; $TeCl_4$), both of which are decomposed by water. The corresponding bromides and iodides are also known. In general, compounds of tellurium are easily reduced to the element. The reduction, however, is not accomplished quite so readily as in the case of selenium compounds.

Estimation.† *A. Gravimetric.* Tellurium is usually weighed as the element, obtained by treating solutions of tellurium compounds (1) with sulphur dioxide; (2) with hydrazine sulphate in ammoniacal solution (Jannasch, Ber. Dtsch. chem. Ges. XXXI, 2377); (3) with hydrazine hydrate or its salts in acid or alkaline solution (Gutbier, Ber. Dtsch. chem. Ges. XXXIV, 2724); (4) with sulphur dioxide and potassium iodide (Frericks, J. pr. Chem. [2] LXVI, 261); (5) with hypophosphorus acid (Gutbier, Zeitsch. anorg. Chem. XXXII, 295); (6) with grape-sugar in alkaline solution (Stolba, *vid.* Kastner, Zeitsch. anal. Chem. XIV, 142); or (7) with acid sodium sulphite or magnesium (*vid.* Experiment 109).

It may be weighed also as the sulphate, ($2TeO_2 \cdot SO_3$),

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* A monoxide, (TeO), also has been described.

† See Gutbier, Studien über das Tellur, pub. by Hirschfeld, Leipzig, 1902; Mac Ivor, Chem. News LXXXVII, 17, 162.

obtained by treating elementary tellurium with a mixture of nitric and sulphuric acids and evaporating (Metzner, Ann. Chim. Phys. [7] XV, 203).

B. Volumetric. Tellurium may be estimated volumetrically (1) by the reduction of telluric acid to tellurous by means of potassium bromide in sulphuric acid solution, ($H_2TeO_4 + 2HBr = H_2TeO_3 + H_2O + Br_2$), the bromine being passed into potassium iodide, and the iodine estimated by standard thiosulphate (Gooch and Howland, Amer. Jour. Sci. [3] XLVIII, 375); (2) by the reducing action of strong hydrochloric acid upon soluble tellurates, chlorine being set free and passed into potassium iodide with liberation of iodine, as above; (3) by the action of standard potassium iodide solution upon a solution of tellurous acid containing twenty-five per cent. by volume of strong sulphuric acid, ($H_2TeO_3 + 4H_2SO_4 + 4KI = TeI_4 + 4KHSO_4 + 3H_2O$), tellurous iodide being precipitated as a black, curdy mass, which, when shaken, separates in such a manner that the point when precipitation ceases can easily be detected; the quantity of tellurium present is calculable from the quantity of potassium iodide used (Gooch and Morgan, Amer. Jour. Sci. [4] II, 271); (4) by the oxidation of tellurous acid by means of standard potassium permanganate in acid or alkaline solution (Norris and Fay, Amer. Chem. Jour. XX, 278; Gooch and Peters, Amer. Jour. Sci. [4] VIII, 122).

Separation.* From the elements not easily reduced from their compounds to elementary form, tellurium may be separated in general by the action of sulphur dioxide in faintly acid solution; this precipitates elementary tellurium. From bismuth tellurium is separated by the action of potassium sulphide upon the precipitate thrown down from solutions by hydrogen sulphide,—the tellurium dis-

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* See Gutbier, Studien über das Tellur.

solving. From antimony the separation may be accomplished (1) by hydrazine hydrate, the tellurium being precipitated (Gutbier, Zeitsch. anorg. Chem. XXXII, 260); (2) by treatment of a solution of sulpho-tellurite and sulpho-antimonite with 20% hydrochloric acid in the presence of tartaric acid, the tellurium separating out (Muthmann and Schröder, Zeitsch. anorg. Chem. XIV, 433). From silver tellurium is separated by hydrochloric acid, the silver being precipitated; from gold by the action of heat on the two metals, tellurium being volatilized; from mercury by the action of phosphorus acid upon a cold dilute hydrochloric acid solution of the salts, mercurous chloride being precipitated.

From selenium tellurium may be separated (1) by hydroxylamine in strong hydrochloric acid solution, the selenium being precipitated (Jannasch and Müller, Ber. Dtsch. chem. Ges. XXXI, 2388); (2) by sulphur dioxide in strong hydrochloric acid solution, selenium being precipitated (Keller, Jour. Amer. Chem. Soc. XIX, 771, and XXII, 241); (3) by fusion of the elements with potassium cyanide in the presence of hydrogen, tellurium being precipitated when air is passed through a solution of the melt; (4) by the action of ferrous sulphate (*vid.* Experiment 109); (5) by the greater volatility of the bromide of selenium (Gooch and Peirce, Amer. Jour. Sci. [4] I, 181).

EXPERIMENTAL WORK ON TELLURIUM.

Experiment 109. *Extraction of tellurium from flue-dust, or from waste products from the electrolytic refining of copper.* Treat about 10 grm. of the material with strong commercial hydrochloric acid until nothing further dissolves, and filter. To a small portion of the filtrate add ferrous sulphate, and warm gently. The presence of selenium will be indicated by a reddish precipitate. If selenium has thus been shown to

be present, take about 5 cm.[3] of the original filtrate, precipitate the selenium and tellurium by acid sodium sulphite or by magnesium, wash this precipitate, return it to the remainder of the filtrate, and heat to boiling. The selenium present will be precipitated by the tellurium. Remove the selenium by filtration and set it aside for later use (*vid.* Experiment 119). From the filtrate precipitate the tellurium by acid sodium sulphite or by magnesium (Crane, Amer. Chem. Jour. XXXIII, 408).

Experiment 110. *Action of strong sulphuric acid upon tellurium.* To a small amount of elementary tellurium add a few cm.[3] of strong sulphuric acid and warm. Note the reddish-violet color. This reaction constitutes a good test for tellurium.

Experiment 111. *Preparation of tellurium dioxide*, (TeO_2). To a small amount of elementary tellurium add nitric acid, evaporate to dryness, and heat gently.

Experiment 112. *Formation of an alkali tellurite*, ($\overset{I}{R}_2TeO_3$). Dissolve a little tellurium dioxide in a solution of sodium or potassium hydroxide.

Experiment 113. *Formation of telluric acid*, (H_2TeO_4). To a solution of an alkali tellurite add sulphuric acid until the precipitate first formed dissolves. Then add gradually a solution of potassium permanganate until no further bleaching action is noticed.

Experiment 114. *Reduction of telluric acid.* To a solution of telluric acid prepared in the previous experiment add a little potassium bromide and sulphuric acid, and boil. Note the evolution of bromine and the reduction to tellurous acid.

Experiment 115. *Precipitation of tellurous iodide*, (TeI_4). To a solution of an alkali tellurite add sulphuric acid until the precipitate first formed dissolves. Then add a few drops of a solution of potassium iodide. Note the black precipitate.

Experiment 116. *Precipitation of elementary tellurium.* Try the action of the following reducing agents upon separate portions of an acid solution containing tellurium: stannous chloride, hydrogen sulphide,* sulphurous acid, magnesium, and acid sodium sulphite (*vid.* Experiment 109).

Experiment 117. *Action of tellurium compounds before the blowpipe.* Heat on charcoal a small amount of a tellurium compound. Note the white sublimate and the green color imparted to the reducing flame.

Experiment 118. *Negative test of tellurium.* Try the action of ferrous sulphate upon an acidified solution of a tellurite.

SELENIUM, Se, 79.1.

Discovery. For some time previous to the discovery of selenium a red deposit had been noticed in the lead chambers used in the manufacture of sulphuric acid at Gripsholm in Sweden. The deposit was present when the sulphur employed had been prepared from pyrites from Fahlun, Sweden, but was seldom observed when the sulphur had been obtained from other sources. At first the unknown substance was supposed to be sulphur. When it was burned, an odor as of decayed cabbage was given off, and this was supposed to be caused by the presence of tellurium sulphide, although no tellurium could be extracted from the material. In 1817 Berzelius, having become a shareholder in the acid works, examined the red deposit, and in a short time he announced the discovery of a new element. Because of its frequent association with tellurium, and its many points of similarity to that element, he named it Selenium, from σελήνη, the *moon* (Annal. der Phys. u. Chem. (1818) XXIX, 229).

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* Some authors give TeS_2 as the constitution of the precipitate by hydrogen sulphide.

Occurrence. Selenium is found usually in combination with the metals, as in the following minerals:

Clausthalite, PbSe,	contains......	27–28% Se
Tiemannite, HgSe,	"	25–29% "
Guanajuatite, Bi_2Se_3,	"	24–34% "
Naumannite, $(Ag_2,Pb)Se$,	"	27–30% "
Berzelianite, Cu_2Se,	"	39–40% "
Lehrbachite, PbSe·HgSe,	"	24–28% "
Eucairite, $Cu_2Se \cdot Ag_2Se$,	"	31–32% "
Zorgite, *vid.* Clausthalite,	"	29–34% "
Crookesite, $(Cu,Tl,Ag)_2Se$,	"	30–33% "
Onofrite, Hg(S,Se),	"	4– 6% "
Galenobismutite, $PbBi_2S_4$,	"	0–14% "
Durdenite, $Fe_2(TeO_3)_3 \cdot 4H_2O$,	"	1– 2% SeO_2
Chalcomenite, $CuSeO_3 \cdot 2H_2O$,	"	48–49% "
Tellurium (native), Te,	"	6– 7% Se
Selen-sulphur, xSe·yS,	"	35–66% "
Selen-tellurium, 3Te·2Se,	"	29–30% "

Extraction. Selenium salts may be extracted from flue-dust by the following methods:

(1) The soluble material is dissolved by treatment with water, and the selenium is extracted from the residue by aqua regia (Berzelius, *vid.* Experiment 119).

(2) The seleniferous material is digested with a solution of potassium cyanide at a temperature of 80°–100° C. until the red color has changed to gray, (KSeCN). The selenium goes into solution and may be precipitated by hydrochloric acid (Pettersson, Ber. Dtsch. chem. Ges. VII, 1719).

(3) The flue-dust or mineral is fused with sodium carbonate, and the selenium is extracted with water as sodium selenide and selenite, (Na_2Se; Na_2SeO_3).

The Element. *A. Preparation.* Selenium in the elementary condition may be prepared by the action (1) of sulphur dioxide, zinc, or iron, upon selenious acid (Berzelius); (2) of hydrochloric acid upon sodium seleno-sulphite (Pettersson); (3) of potassium iodide, sodium thiosulphate, etc., upon selenious acid.

B. Properties. Like sulphur, selenium is known in several allotropic modifications,* and may be either soluble or insoluble in carbon disulphide. In soluble form selenium is a red powder which softens at 50°–60° C., is partly fluid at 100° C. and is completely fused at 250° C. After it has been melted it remains in a plastic condition for a long time and has a metallic luster. Its specific gravity is 4.2 to 4.3. From a warm solution in carbon disulphide the element separates in red, monoclinic, crystalline plates, and from a cold solution in orange-red monoclinic crystals of different type. The specific gravity of these crystalline varieties is 4.4 to 4.5. Selenium insoluble in carbon disulphide may be obtained by allowing the element to cool very slowly after it has been heated to a higher temperature than 130° C., or by allowing the oxygen of the air to act upon selenides in aqueous solution. Under these conditions the element assumes the so-called metallic form, crystallizes in steel-gray hexagonal crystals, and becomes isomorphous with tellurium. Metallic selenium melts at 217° C. without previous softening. Its specific gravity is 4.8.

Selenium boils at 700° C., yielding a dark-yellow vapor which, when condensed and cooled, assumes a form similar to flowers of sulphur; this is called flowers of selenium. The element is soluble in sulphuric acid, giving a green solution, and is oxidized by nitric acid to selenious acid, (H_2SeO_3).

* For a recent discussion of these modifications see Saunders, Jour. Phys. Chem. (1900) IV, 423.

It combines with metals to form selenides. When heated in air or oxygen it burns with a blue flame and goes over to the dioxide, (SeO_2). It is a poor conductor of heat and electricity.

Compounds. *A. Typical forms.* The following compounds of selenium may be considered typical:

Oxides.		SeO_2	SeO_3
Chlorides.	Se_2Cl_2	$SeCl_4$	
		$SeCl_3Br$	
Oxychloride.		$SeOCl_2$	
Bromides.	Se_2Br_2	$SeBr_4$	
		$SeClBr_3$	
Iodides.	Se_2I_2	SeI_4	
Seleno-sulphite. . . .	$SeSO_3$		
Alums.			$\overset{I}{R}_2Al_2(SeO_4)_4+24H_2O$
Thioselenic acid. . .			H_2SSeO_3
Thioseleniate.			K_2SSeO_3
Cyanides.	$(CN)_2Se$		
	$(CN)_2Se_3$		
	$H(CN)Se$		
	$K(CN)Se$		
	$\overset{II}{R}(CN)Se_2$		
Nitride.	N_2Se		
Phosphides.	P_4Se_3		
	P_2Se_5		
Selenides.	H_2Se		
	$NiSe$		
	Ag_2Se		
	K_2Se, etc.		
Acids (selenious and selenic)		H_2SeO_3	H_2SeO_4
Salts (selenites and seleniates)		$\overset{I}{R}_2SeO_3$	$\overset{I}{R}_2SeO_4$

B. Characteristics. The compounds of selenium closely resemble those of tellurium, both in structure and in behavior

toward reagents. They are, however, rather more sensitive to the action of reducing agents, and readily precipitate the red, amorphous variety of the element, which tends to become black when heated. Hydrogen selenide is a gas which acts like hydrogen sulphide and hydrogen telluride, and precipitates the selenides ($\overset{I}{R}_2Se$). By the treatment of elementary selenium with nitric acid or aqua regia and evaporation to dryness, selenious oxide, (SeO_2), is formed, which dissolves in water, forming selenious acid, (H_2SeO_3). By the action of powerful oxidizing agents, such as chlorine, bromine, or potassium permanganate, selenious acid may be oxidized to selenic acid, (H_2SeO_4), which is not reduced by sulphur dioxide. These acids form salts of the types $\overset{I}{R}_2SeO_3$ and $\overset{I}{R}_2SeO_4$. By the action of reducing agents, such as sulphur dioxide or ferrous sulphate, red amorphous selenium may be readily precipitated from selenious acid. Two chlorides, (Se_2Cl_2; $SeCl_4$), and the corresponding bromides and iodides are known. When selenium is heated, a characteristic, penetrating odor is given off which has been variously described as like that of garlic, decayed cabbage, and putrid horseradish. This odor is caused by the formation of small amounts of the hydride.

Estimation. *A. Gravimetric.* Selenium is generally weighed as the element, obtained by treating solutions of its compounds (1) with sulphurous acid in hydrochloric acid solution; (2) with potassium iodide in acid solution (Peirce, Amer. Jour. Sci. [4] I, 416); (3) with hypophosphorus acid in alkaline solution (Gutbier and Rohn, Zeitsch. anorg. Chem. XXXIV, 448). Other reducing agents may be used.

B. Volumetric. Selenium may be determined volumetrically (1) by oxidizing selenious acid to selenic by means of standard potassium permanganate in sulphuric acid solution, using an excess of permanganate, and titrat-

ing back with oxalic acid (Gooch and Clemons, Amer. Jour. Sci. [3] L, 51); (2) by reducing selenic or selenious acid by means of potas ium iodide in hydrochloric acid solution, ($SeO_2 + 4HI = 2H_2O + Se + 2I_2$; $SeO_3 + 6HI = 3H_2O + Se + 3I_2$), and determining by appropriate means the iodine set free (Muthmann and Schaefer, Ber. Dtsch. chem. Ges. XXVI, 1008; Gooch and Reynolds, Amer. Jour. Sci. [3] L, 254); (3) by reducing selenic acid to selenious by boiling with hydrochloric acid, ($SeO_3 + 2HCl = SeO_2 + H_2O + Cl_2$), then passing the free chlorine into potassium iodide, and determining the iodine set free (Gooch and Evans, Amer. Jour. Sci. [3] L, 400); (4) by employing potassium bromide and sulphuric acid instead of hydrochloric acid in (3) (Gooch and Scoville, Amer. Jour. Sci. [3] L, 402); (5) by boiling a solution of selenious acid with sulphuric acid, a known amount of potassium iodide, and an excess of arsenic acid; the reduction of the selenious acid will decrease the reduction of arsenic acid; the quantity of arsenious acid present at the close of the action may be measured, after neutralization with potassium bicarbonate, by standard iodine (Gooch and Peirce, Amer. Jour. Sci. [4] I, 31); (6) by the reduction of selenious acid to elementary selenium by means of standard sodium thiosulphate solution in excess in the presence of hydrochloric acid,—the excess of thiosulphate being determined by standard iodine solution (Norris and Fay, Amer. Chem. Jour. XVIII, 703; Norton, Amer. Jour. Sci. [4] VII, 287); (7) by boiling elementary selenium with ammonia and standard silver nitrate solution, acidifying with nitric acid, and determining the excess of silver nitrate by ammonium sulpho-cyanide, with ferric alum as indicator; the quantity of selenium present is calculable from the quantity of silver nitrate used, as is shown in the following equation: $4AgNO_3 + 3Se + 3H_2O = 2Ag_2Se + H_2SeO_3 + 4HNO_3$ (Friedrich, Zeitsch. angew. Chem. XV, 852).

Separation. Selenium is separated, together with tellurium, from other elements by methods given under Tellurium. Methods of accomplishing the separation of these two elements from each other have also been described.

EXPERIMENTAL WORK ON SELENIUM.

Experiment 119. *Extraction of selenium from* (1) *flue-dust and* (2) *seleniferous residues from the electrolytic refining of copper.* (1) Treat about 25 grm. of the washed flue-dust with aqua regia as long as any evidence of action is observed, and evaporate to dryness. Extract the residue with about 25 $cm.^3$ of strong common hydrochloric acid, and filter. To the filtrate add about a gram of dry ferrous sulphate, and warm gently if necessary. Filter off the red amorphous selenium.

(2) To free the selenium obtained in Experiment 109 from the excess of tellurium present (*a*) treat the material with hydrochloric acid and either a little chlorine or a drop of nitric acid. Precipitate the selenium by ferrous sulphate. (*b*) Or warm the material with a dilute solution of potassium cyanide. The selenium goes into solution as potassium seleno-cyanide and may be precipitated by acidifying the solution with hydrochloric acid.

Experiment 120. *Preparation of selenium dioxide*, (SeO_2). To a small amount of elementary selenium add nitric acid until the oxidation is shown to be complete by the cessation of the evolution of red fumes (oxides of nitrogen). Evaporate to dryness and warm gently. The white residue is selenium dioxide. Dissolve this in a little water to form selenious acid, (H_2SeO_3).

Experiment 121. *Precipitation of barium selenite*, ($BaSeO_3$). To a little selenious acid add a few drops of

a barium salt in solution. Test the action of hydrochloric acid upon the precipitate.

Experiment 122. *Formation of selenic acid*, (H_2SeO_4). To a few cm.[3] of selenious acid add first a small amount of sulphuric acid and then a solution of potassium permanganate until the purple color is permanent. Bleach by the careful addition of oxalic acid.

Experiment 123. *Reduction of selenic acid to selenious.* Add to a given volume of selenic acid half as much strong hydrochloric acid and boil to about two thirds of the total volume. Note the evolution of chlorine. Test by starch iodide paper.

Experiment 124. *Precipitation of elementary selenium.* Try the action of the following reducing agents upon dilute selenious acid: sulphur dioxide, hydrogen sulphide, acid sodium sulphite, potassium iodide, stannous chloride, ferrous sulphate.

Experiment 125. *Solvent action of carbon disulphide upon selenium.* To a little dry, washed, amorphous selenium add carbon disulphide. Filter, and allow the filtrate to evaporate.

Experiment 126. *Solvent action of potassium cyanide upon selenium.* To a small amount of the red amorphous selenium add a few cm.[3] of a dilute solution of potassium cyanide (poison!), warm gently, and filter. To the filtrate add hydrochloric acid.

Experiment 127. *Behavior of selenium when subjected to heat.* Heat a small amount of elementary selenium on a glass rod. Note the odor, and the color of the flame.

Experiment 128. *Action of strong sulphuric acid upon selenium.* To a small amount of elementary selenium add a few cm.[3] of strong sulphuric acid and warm. Note the color. Compare with tellurium (*vid.* Experiment 110).

PLATINUM, Pt, 194.8.

Discovery. In the year 1750 William Watson presented to the Royal Society a communication from William Brownrigg in which was described a "semi-metal called Platina di Pinto" found in the Spanish West Indies. Watson stated that, so far as he knew, no previous mention had been made of this substance except by Don Antonio de Ulloa in the history of his voyage to South America, published in Madrid in 1748 (Phil. Trans. Roy. Soc. (1750) XLVI, 584). However, an earlier discovery is suggested by a statement of Scaliger in 1558, who, in combating the opinion of Cardanus, that all metals are fusible, declared that an infusible metallic substance existed in the mines of Mexico and Darien. As platinum is found in those countries, it is probably the metal referred to. The name Platinum is derived from the Spanish *platina*, the diminutive of *plata*, *silver*.

Occurrence. Platinum occurs alloyed with the various metals of its group—palladium, osmium, iridium, etc.—and associated with other metals, as iron, lead, copper, titanic iron, etc. It is found chiefly in the Ural Mountains, but also in Brazil, Mexico, Borneo, California, North Carolina, and elsewhere. It comprises from fifty to eighty per cent. of the alloys in which it occurs. Platinum is found combined in the mineral sperrylite, $PtAs_2$, which contains about fifty-three per cent. of the metal.

Extraction. Platinum may be extracted from its alloys by the following methods:

(1) *Fusion process.* The material is fused with sulphide of lead. The iron present combines with the sulphur. The platinum alloys with the lead, while the osmium and iridium do not. The lead-platinum alloy is separated from the mass and cupelled. The platinum is left (Deville and Debray).

(2) *Wet process.* The pulverized alloy is heated in a porcelain dish with aqua regia as long as action continues. The solution obtained is nearly neutralized with calcium hydroxide, and the iron, copper, rhodium, iridium, and part of the palladium separate. After the removal of these, the filtrate is evaporated to dryness and the residue is ignited and treated with water and hydrochloric acid. The platinum, with traces of the platinum metals, remains.

The Element. *A. Preparation.* As extracted from its alloys, platinum is in the elementary condition (*vid.* Extraction).

B. Properties. In its usual form, elementary platinum is a grayish-white metal which is very malleable and ductile, but fusible only in the oxyhydrogen blowpipe or by means of the electric current. At no temperature is it oxidized by water or oxygen, or attacked by the simple acids. It is soluble, however, in aqua regia. Platinum is not acted upon by sulphur alone, but if alkalies are present with the sulphur some action takes place. It is attacked also when heated with potassium nitrate. Its specific gravity is 21.48.

Besides the ordinary form, the element platinum is known to exist in two allotropic conditions: (1) spongy platinum, obtained by the ignition of ammonium chloroplatinate, and (2) platinum-black, obtained by reducing acid solutions of platinum salts. In both of these forms platinum condenses gases on its surface.

Compounds. *A. Typical forms.* The following may be regarded as typical compounds of platinum:

Oxides	PtO	Pt_3O_4	PtO_2
Chlorides	$PtCl_2$		$PtCl_4$
Double chlorides	$PtCl_2 \cdot SrCl_2 + 6H_2O$, etc.		$PtCl_4 \cdot 2AgCl$, etc.
Bromides	$PtBr_2$		$PtBr_4$
Double bromides	$PtBr_2 \cdot 2KBr$, etc.		$PtBr_4 \cdot SrBr_2 + 10H_2O$
Iodides	PtI_2		PtI_4

Double iodides		$PtI_4 \cdot 2KI$, etc.
Fluorides	PtF_2	PtF_4
Sulphides	PtS	PtS_2
Oxysulphide		$PtOS$
Sulpho salts		R_2PtS_6
Sulphites		$PtSO_3 \cdot \overset{I}{R}_2SO_3$; $PtSO_3 \cdot 2\overset{I}{R}Cl$
Nitrites		$\overset{I}{R}_2(NO_2)_4Pt$
Iodonitrites		$\overset{I}{R}_2(NO_2)_2I_2Pt$
Cyanide	$Pt(CN)_2$	
Hydro-platino-cyanic acid	$H_2Pt(CN)_4$	
Platino-cyanides	$\overset{I}{R}_2Pt(CN)_4$; $\overset{II}{R}Pt(CN)_4$, typical	
Chloroplatinic acid		H_2PtCl_6
Chloroplatinates		$\overset{I}{R}_2PtCl_6$; $\overset{II}{R}PtCl_6$, typical

B. Characteristics. The compounds of platinum may be divided into two classes, of which the platinous and platinic oxides, (PtO; PtO_2), serve as types. The salts of the lower condition of oxidation are usually colorless or reddish brown; they give with hydrogen sulphide or ammonium sulphide a dark-brown precipitate of platinous sulphide, (PtS), which is soluble in ammonium sulphide. They are decomposed at red heat, and are slowly reduced to metallic platinum when boiled with ferrous sulphate. The salts of the higher condition of oxidation have a yellow or brown color, and like the platinous salts they are decomposed at red heat. Metals in general and organic matter precipitate platinum from solutions of platinic salts. The brownish-gray platinic sulphide, (PtS_2), is precipitated by the action of hydrogen sulphide upon a solution of chloroplatinic acid, (H_2PtCl_6); this sulphide dissolves slowly in ammonium sulphide. Salts of potassium and ammonium act upon chloroplatinic acid precipitating the corresponding salts of that acid, ($\overset{I}{R}_2PtCl_6$). When platinous chloride dissolves in potassium cyanide, platinum potas-

sium cyanide is formed, $(K_2Pt(CN)_4 + 4H_2O)$. Many salts of this type are known.

The platinum-ammonium compounds comprise a large number of complex salts of the following types:

(*a*) The platosamines, $PtR_2(NH_3)_4$; $PtR_2(NH_3)_3$; $PtR_2(NH_3)_2$; $PtR_2(NH_3)$; and (*b*) the platinamines, $PtR_4(NH_3)_4$; $PtR_4(NH_3)_3$; $PtR_4(NH_3)_2$; $PtR_4(NH_3)$.

In the above formulæ R may stand for OH, Cl, Br, I, or NO_3. These compounds are formed by the action of ammonia upon the platinum salts.

Potassium iodide gives a red-brown color to very dilute solutions of platinum salts.

Estimation. *A. Gravimetric.* Platinum is generally weighed as the metal, obtained (1) by precipitation from solutions of compounds by means of appropriate reducing agents, such as formic acid, alcohol in alkaline solution, or magnesium (Atterberg, Chem. Ztg. XXII, 538); (2) by precipitation of the sulphide and ignition; (3) by precipitation of ammonium or potassium chloroplatinate, and decomposition by heat into the metal and the volatile or soluble alkali chloride.

B. Volumetric. Platinum may be estimated volumetrically by reducing the tetrachloride by means of potassium iodide, $(PtCl_4 + 4KI = PtI_2 + I_2 + 4KCl)$, and determining by standard sodium thiosulphate the iodine thus liberated (Peterson, Zeitsch. anorg. Chem. XIX, 59).

Separation. From most other elements platinum may be separated by the action of reducing agents in precipitating the metal from solutions. From the metals with which it is most often found associated it may be separated by the following methods: from gold (1) by the action of ammonium chloride upon the chlorides, ammonium chloroplatinate being precipitated; (2) by the action of hydrogen dioxide and sodium hydroxide upon cold solutions, the gold being precipitated (Vanino and Seeman, Ber. Dtsch.

chem. Ges. XXXII, 1968); (3) by the action of oxalic acid or ferrous salts, gold being again precipitated (Hoffmann and Krüss, Zeitsch. anal. Chem. XXVII, 66; Bettel, Chem. News LVI, 133); from silver by heating the metals with concentrated sulphuric acid, silver dissolving (Richards, The Analyst, XXVII, 265); from mercury by ignition of the metals, mercury being volatilized.

The separation of platinum from the other platinum metals is so involved with the separation of these from each other that the whole subject will be briefly considered in this place. The following methods have been suggested. (1) The ore is first treated with chlorine water, which extracts the gold, then with dilute aqua regia, which dissolves the platinum, palladium, and rhodium. From this solution the platinum is precipitated by ammonium chloride and alcohol; and from the filtrate, after neutralization with sodium carbonate, the palladium is precipitated as the cyanide by mercury cyanide. The residue from the aqua regia treatment, containing osmium, iridium, and ruthenium, is heated in air. Osmium is volatilized as the tetroxide, ruthenium sublimes as the dioxide, and iridium is left (Pirngrüber, J. B. (1888), 2560; Wyatt, Eng. and Min. J. XLIV, 273). (2) A neutral or acid solution of the platinum metals, gold, and mercury, containing chlorine, is treated with dilute nitric acid and heated to boiling in a retort; osmic tetroxide distils. The solution is cooled, and shaken with ether, which withdraws the chloride of gold. After the removal of the ether and gold by means of a separating funnel the remaining solution is treated with ammonium acetate and boiled with formic acid. This treatment precipitates all the metals, which are then heated in a current of hydrogen to volatilize the mercury. The remaining metals are mixed with sodium chloride and heated with moist chlorine, and the mass is extracted with water. If there is any residue at this point it will probably

be found to be iridium and ruthenium. The solution is treated with concentrated ammonium chloride as long as any precipitate forms. This precipitate consists of the double chlorides of ammonium with platinum, iridium, and ruthenium respectively, palladium and rhodium remaining in solution. The precipitate is dissolved in warm water and treated with hydroxylamine, which reduces the iridium and ruthenium to the condition of the sesquichlorides; upon the addition of ammonium chloride platinum is precipitated as the chloroplatinate. The hydroxylamine filtrate is evaporated, the residue is heated in the presence of hydrogen and fused with potassium hydroxide and nitrate, the mass is cooled and extracted with water. Ruthenium dissolves as potassium ruthenate, (K_2RuO_4), and iridium remains as the hydrate, ($Ir(OH)_3$). The solution containing rhodium and palladium is evaporated slowly to dryness in the presence of an excess of ammonia, and the residue is dissolved in the smallest possible amount of a warm, dilute ammoniacal solution. Upon cooling, the rhodium separates as a complex chloride, ($Rh(NH_3)_5Cl_3$), and the palladium remains in solution (Mylius and Dietz, Ber. Dtsch. chem. Ges. XXXI, 3187). (3) Gold is removed by means of dilute aqua regia. By treatment with concentrated aqua regia platinum, palladium, rhodium, ruthenium, and part of the iridium are then dissolved, while an insoluble alloy of osmium and iridium in the form of grains or plates remains. This alloy is mixed with sodium chloride and the mixture is heated in a tube with chlorine. Osmium tetroxide, (OsO_4), distils, and sodium-iridium chloride, (Na_2IrCl_6), remains (Wöhler, Pogg. Annal. XXXI, 161). To the solution of the other platinum metals in aqua regia ammonium chloride is added. The precipitate, consisting of the double salts of platinum and iridium, may by ignition be converted into iridium-bearing platinum sponge (used in the manufacture of platinum vessels). To the filtrate iron or copper is added,

which throws down the palladium, rhodium, and ruthenium as a metallic powder. From this mixture palladium and the iron or copper are dissolved by nitric acid, and the solution is then shaken with mercury, which removes the palladium (von Schneider, Liebig Annal. v, 264, suppl.). The mixture of rhodium and ruthenium remaining is heated with sodium chloride at low redness in a current of chlorine and the mass is extracted with water. This liquid is boiled with potassium nitrite and enough potassium carbonate to make the solution faintly alkaline. It is then evaporated to dryness and the residue is pulverized and extracted with absolute alcohol. The rhodium remains undissolved as a double nitrite of potassium and rhodium, ($K_6Rh_2(NO_2)_{12}$, while the ruthenium dissolves, also as a double nitrite with potassium, ($Ru(NO_2)_6 \cdot 6KNO_2$).

Platinum may be separated from palladium (1) by the action of warm dilute nitric acid upon the metals, palladium dissolving; (2) by the action of a strong solution of ammonium chloride and alcohol upon the double potassium salts, the palladium salt being soluble (Cohn and Fleissner, Ber. Dtsch. chem. Ges. XXIX, R. 876); from iridium (1) by electrolysis, the platinum being precipitated (Smith, Amer. Chem. Jour. XIV, 435); (2) by the action of potassium nitrite, sodium carbonate, and boiling water upon the double potassium salts, iridium being reduced to the condition of the sesquichloride and dissolved (Gibbs, Amer. Jour. Sci. [2] XXXIV, 347); from osmium by heating in the presence of oxidizing material, osmium tetroxide being formed and volatilized; from ruthenium by treating potassium chloroplatinate and the corresponding ruthenium salt with cold water, the ruthenium salt dissolving (Gibbs, *loc. cit.*); from rhodium (1) by the method described for the separation from ruthenium; or (2) by the action of concentrated solutions of the alkali chlorides upon these salts, the rhodium dissolving (Gibbs, *loc. cit.*).

EXPERIMENTAL WORK ON PLATINUM.

Experiment 129. *Preparation of chloroplatinic acid from laboratory residues.* Boil the residues consisting of potassium chloroplatinate, etc., with a solution of sodium carbonate and add a little alcohol. The platinum is deposited as a black powder. Wash the powder, first with hot water, then with hot hydrochloric acid; dry it, dissolve it in aqua regia, evaporate the liquid, adding a little hydrochloric acid from time to time to remove the nitric acid, until the point of crystallization is reached.

Experiment 130. *Precipitation of the chloroplatinates of ammonium, potassium, cæsium, rubidium, and thallium,* ($\overset{\mathrm{I}}{R}_2PtCl_6$). To separate portions of a solution of chloroplatinic acid add salts of ammonium, potassium, cæsium, rubidium, and thallium in solution. Note the comparative insolubility of the new compounds in water and in alcohol.

Experiment 131. *Precipitation of platinic sulphide,* (PtS_2). To a solution of chloroplatinic acid add a little hydrogen sulphide, and warm.

Experiment 132. *Precipitation of elementary platinum.* (*a*) To a solution of a platinum salt add sodium carbonate to alkaline reaction; add also a few drops of alcohol and boil.

(*b*) Try the action of oxalic acid upon a platinum salt in solution.

Experiment 133. *Action of acids upon platinum.* Try separately the action of strong hydrochloric and nitric acids upon metallic platinum. Note the effect of a mixture of the two acids upon the metal.

Experiment 134. *Test for platinum in solution.* To a very dilute solution of a platinum salt free from chlorine add a small crystal of potassium iodide. Note the color.

THE PLATINUM METALS

OTHER THAN PLATINUM.

Occurring almost invariably associated with platinum and usually alloyed with it are small quantities of certain rare elements which, together with platinum, comprise the group of so-called Platinum Metals. These very rare elements are the following:

Palladium, Pd, 106	Osmium, Os, 191
Iridium, Ir, 193	Rhodium, Rh, 103
Ruthenium, Ru, 101.7	

Discovery. In 1803, in the course of the purification of a considerable quantity of crude platinum, Wollaston isolated a new metal which he named Palladium, in honor of the discovery by Olbers of the planetoid Pallas. The newly discovered element was brought to the attention of scientists anonymously through a dealer's advertisement, which offered "palladium or new silver" for sale. Much discussion as to the nature of the substance ensued, Chenevix, in particular, holding it to be an alloy of platinum and mercury. In 1805 Wollaston confessed to the discovery and naming of the metal (Phil. Trans. Roy. Soc. (1803) XCIII, 290; ibid. (1805) XCV, 316; Nicholson's J. (1805) X, 204).

The same year that palladium was discovered, Smithson Tennant found that "the black powder which remained after the solution of platina did not, as was generally believed, consist chiefly of plumbago, but contained some unknown metallic ingredients." In 1804 he presented to the Royal Society as the result of his study a communication announcing the discovery of two new metals, Iridium, named "from the striking variety of colors which it gives while dissolving in marine acid," and Osmium, so called because of the

penetrating odor (*οσμή, odor*) of the acid obtained from the oxidation of the element when it is heated in a finely divided condition (Phil. Trans. Roy. Soc. (1804) XCIV, 411).

A few days after Tennant's communication, Wollaston announced the discovery of an element in the "fluid which remains after the precipitation of platina by sal ammoniac," and suggested the name Rhodium (*ῥόδιος, rose-like*), "from the rose color of a dilute solution of the salts containing it" (Phil. Trans. Roy. Soc. (1804) XCIV, 419).

In 1826 Osann claimed the discovery of three new elements in platinum alloys. These he named Ruthenium, Polinium, and Pluranium (Pogg. Annal. VIII, 505; Amer. Jour. Sci. XVI, 384). Later he withdrew the claim. In 1844 Claus found that there was an unknown metal in the mixture of substances which had been called by Osann "ruthenium oxide," and for it he retained the name ruthenium, derived from Ruthenia, i.e. Russia, where the substance was first found (Pogg. Annal. LXIV, 192, 208; Amer. Jour. Sci. XLVIII, 401).

Occurrence. The very rare platinum metals, as has been already stated, are found in general in platinum-bearing material. Palladium and iridium sometimes occur native; the others always in alloys or in combination.

		% Pd	% Os	% Ir	% Rh	% Ru
Native platinum	**contains**	0.1–3.1		traces–4.2	traces	0.2–3.4
" iridium	"	0.4–0.8		27–76.8		*circa* 7
Palladium gold	"	5–10				
Iridosmine	"		17–48	40.7	0.5–12.3	0.2–6
Laurite, RuS_2	"		*circa* 3			65
Rhodium gold	"				34–43	

Extraction. For methods of extraction of the very rare platinum metals see Extraction and Separation of Platinum.

The Elements. I. PALLADIUM. *A. Preparation.* Elementary palladium may be obtained (1) by heating the potassium double chloride with hydrogen (Roessler); (2) by

heating the iodide with hydrogen; and (3) by heating the chloride or cyanide.

B. Properties. Palladium is a ductile, malleable, white metal which looks like platinum. It may be partially oxidized before the oxyhydrogen blowpipe. It is soluble in strong nitric, hydrochloric, and sulphuric acids, and easily soluble in aqua regia. It fuses at a lower temperature than any other of the platinum metals. In spongy form it has the power of absorbing gases. Its specific gravity is 11.4–11.8. Because of the color and hardness of palladium and its unalterability in the air it is used for the graduated surfaces of fine astronomical instruments. It may be distinguished from the other platinum metals by the comparative ease with which it dissolves in nitric acid.

II. Osmium. *A. Preparation.* The element osmium may be prepared (1) by heating the amalgam in the presence of hydrogen (Berzelius); (2) by heating the sulphide in a closed coke crucible; (3) by passing the vapor of the tetroxide mixed with carbon dioxide and carbon monoxide through a heated porcelain tube; (4) by passing the vapor of the tetroxide through a heated porcelain tube containing finely divided carbon (Deville and Debray); (5) by igniting osmyldiamine chloride, ($Os(NH_3)_4O_2Cl_2$), in a current of hydrogen.

B. Properties. Osmium, the heaviest of the platinum metals, is a bluish substance, crystals of which are harder than glass. In the compact form it is insoluble in all acids and in aqua regia, and is rendered soluble only by fusion with nitrates. The amorphous modification is slowly soluble in nitric acid and in aqua regia. The specific gravity of the compact and amorphous modifications is 21.3; of the crystalline form 22.4. In the alloy iridosmine the element is employed for compass bearings and for the tips of gold pens.

III. Iridium. *A. Preparation.* Metallic iridium may

be obtained (1) by heating iridium-ammonium chloride, and (2) by heating iridium-potassium chloride with sodium carbonate.

B. Properties. Iridium, a hard, brittle metal, resembles silver and tin in appearance. The ignited form is insoluble in all acids and in aqua regia. The element is partially oxidized, however, by fusion with sodium nitrate, and the fused mass may be dissolved by boiling it with aqua regia. In spongy form iridium has the specific gravity of 15.86; after fusion the specific gravity is 21–22. Elementary iridium is not used in the arts, but its alloy with osmium, as stated above, is employed for compass bearings and for the tips of gold pens; its alloy with platinum is used in the manufacture of laboratory vessels and for standard weights and measures, and an oxide is used in china-painting.

IV. RHODIUM. *A. Preparation.* Elementary rhodium may be prepared (1) by heating ammonium-rhodium sesquichloride; (2) by heating rhodium sesquichloride and sodium in a current of hydrogen; (3) by heating rhodium sulphide to a white heat; and (4) by allowing reducing agents, as formic acid, zinc, iron, alcohol in alkaline solution, hydrogen, etc., to act upon soluble salts.

B. Properties. Rhodium is a grayish-white metal which has the appearance of aluminum. When pure it is almost absolutely insoluble in acids and in aqua regia, but when alloyed it may be dissolved in aqua regia. It is fusible before the oxyhydrogen blowpipe, but more difficultly than platinum. It has the property of absorbing hydrogen. Of all the platinum metals rhodium is most easily attacked by chlorine. Its specific gravity is 11–12. The alloy of rhodium with steel is somewhat used in the arts.

V. RUTHENIUM. *A. Preparation.* The element ruthenium may be obtained (1) by heating the oxide with illuminating-gas, and (2) by heating ruthenium-ammonium-mercury chloride.

B. Properties. Ruthenium is a hard, brittle metal, dark gray to black in color. It is almost completely insoluble in acids and in aqua regia; and osmium alone, of all the platinum metals, is more difficultly fusible. It may be slightly oxidized by fusion with caustic potash and oxidized to a greater degree by fusion with potassium nitrate. The specific gravity of the crystalline form is 12.26; of the melted form 11.4; and of the porous form 8.6.

Compounds. *A. Typical forms.* The following compounds of the platinum metals may be considered typical:

Oxides.	Pd_2O				
	PdO	OsO	IrO?	RhO	RuO
		Os_2O_3	Ir_2O_3	Rh_2O_3	Ru_2O_3
	PdO_2	OsO_2	IrO_2	RhO_2	RuO_2
		(OsO_3)*			(RuO_3)*
		OsO_4			RuO_4
					(Ru_2O_7)*
Chlorides......	$PdCl$				
	$PdCl_2$	$OsCl_2$	$IrCl_2$	$RhCl_2$	$RuCl_2$
		$OsCl_3$	Ir_2Cl_6	Rh_2Cl_6	Ru_2Cl_6
	$PdCl_4$	$OsCl_4$	$IrCl_4$		$RuCl_4$
Bromides.....	$PdBr_2$				
			Ir_2Br_6		
	$PdBr_4$		$IrBr_4$		
Iodides........	PdI_2				
			Ir_2I_6?	Rh_2I_6	Ru_2I_6
			IrI_4		
Sulphides.....	Pd_2S				
	PdS		IrS	RhS	
			Ir_2S_3	Rh_2S_3	Ru_2S_3
	PdS_2	OsS_2	IrS_2		RuS_2
					RuS_3
		OsS_4			
Sulphates.....	$PdSO_4$				
				$Rh_2(SO_4)_3$	
					$Ru(SO_4)_2$
Sulphites......	$PdSO_3 \cdot 3Na_2SO_3$	$OsSO_3$			
			$Ir_2(SO_3)_3$	$Rh_2(SO_3)_3$	
Sulpho salts....	$R_2Pd_3S_4$				
	R_2PdS_3				

* This oxide is known only in combination.

Nitrites.	$Pd(NO_2)_2 \cdot 2KNO_2$		$Ir_2(NO_2)_6 \cdot 6HNO_2$	$Rh_2(NO_2)_6 \cdot 6RNO_2$	$Ru_2(NO_2)_6 \cdot 6RNO_2$
Nitrates.	$Pd(NO_3)_2$			$Rh_2(NO_3)_6$	
Acids and correspond'g salts. . .	H_2PdCl_4; $\overset{I}{R}_2PdCl_4$				
		H_3OsCl_6; $\overset{I}{R}_3OsCl_6$		$\overset{I}{R}_4RhCl_7$; $\overset{I}{R}_3RhCl_6$	H_2RuCl_5
	H_2PdCl_6; $\overset{I}{R}_2PdCl_6$	H_2OsCl_6; $\overset{I}{R}_2OsCl_6$	$\overset{I}{R}_2IrCl_6$		H_2RuCl_6

Characteristics. I. PALLADIUM. The compounds of palladium resemble those of platinum, both in form and in general characteristics. As in the case of platinum, palladium combines with ammonia to form complex salts, and an oxide, (PdO), forms salts with sulphur dioxide and with nitrogen trioxide, (N_2O_3). In general the salts are quite easily reduced to the metal by heating; their solutions resemble a solution of platinic chloride in color. Two oxides, (PdO; PdO_2), are well known, of which the lower forms the more stable compounds. These compounds give a yellowish-brown precipitate with potassium hydroxide. Solutions of palladium salts give with mercuric cyanide a yellowish-white precipitate, ($Pd(CN)_2$); with potassium iodide a black precipitate, (PdI_2), which is soluble in excess of the reagent; and with hydrogen sulphide also a black precipitate, (PdS), insoluble in ammonium sulphide. Mercuric cyanide and potassium iodide are often used as tests for palladium.

II. OSMIUM. Compounds of osmium are known in five degrees of oxidation. The lowest three oxides, (OsO; Os_2O_3; OsO_2), are basic in character, the fourth,* (OsO_3), is acidic, and the fifth, (OsO_4), is also acidic, but it forms

* Known only in salts.

no salts. Three chlorides, ($OsCl_2$; $OsCl_3$; $OsCl_4$), are known, corresponding to the lowest oxides. The metals sodium, potassium, and barium form salts of the type $\overset{I}{R}_2OsO_4$. These salts are readily decomposed, especially by acids, and form the dioxide and the tetroxide. When osmium compounds are heated in the air with oxidizing agents, or are melted with potassium nitrate, the tetroxide is obtained. It is volatile when heated, highly corrosive, and disagreeable like chlorine. It is soluble in water and is reduced by reducing agents. From potassium iodide it frees iodine, and with formic acid to which potassium hydroxide has been added it gives a violet color. With ferrous sulphate it precipitates black osmium hydroxide, ($Os(OH)_4$), and with hydrogen sulphide it brings down the brownish-black sulphide (OsS_4), which is insoluble in ammonium sulphide.

III. IRIDIUM. The compounds of iridium exist chiefly in three conditions of oxidation, of which the di-, tri-, and tetrachlorides may serve as types, ($IrCl_2$; Ir_2Cl_6; $IrCl_4$). The iridium compounds are reduced to the metal when mixed with sodium carbonate and heated in the outer flame of a Bunsen burner. The alkali double chlorides with iridous chloride, ($IrCl_2$), are in general soluble in water. Solutions of iridium salts in the lowest condition of oxidation give with potassium hydroxide a greenish precipitate, which tends to darken when boiled. Reducing agents, as sodium formate, precipitate metallic iridium, and hydrogen sulphide precipitates from the warmed solution a brown iridium sulphide (IrS). By means of oxidizing agents, solutions of iridous salts may be converted into the highest condition of oxidation. From solutions of this latter type potassium hydroxide throws down a dark-brown precipitate of potassium-iridium chloride, ($IrCl_4 \cdot 2KCl$), and hydrogen sulphide precipitates slowly a brown sulphide, (Ir_2S_3). The greater number of iridium compounds are easily reduced by hydrogen on being heated. The pres-

ence of iridium may be detected by the blue color developed when the compound is heated with concentrated sulphuric acid to which ammonium nitrate has been added.

IV. RHODIUM. Although three oxides of rhodium are known and described, (RhO; Rh_2O_3; RhO_2), salts of only two conditions of oxidation are generally found; of these the di- and trichlorides are types, ($RhCl_2$; Rh_2Cl_6). From solutions of rhodium salts reducing agents precipitate the metal. Hydrogen sulphide throws down from a cold solution the sulphide (Rh_2S_3), and from a hot solution the sulphydrate ($Rh_2(SH)_6$). The insolubility of the double chloride of rhodium and sodium, ($Rh_2Cl \cdot 6NaCl$), in water, and of the double nitrate of rhodium and potassium, ($K_6Rh_6(NO_2)_{12}$), in alcohol is made use of in separating the metal from the other members of the group. Rhodium is detected in the presence of the other platinum metals by the yellow solution obtained after fusion with potassium acid sulphate and the change of color to red upon the application of hydrochloric acid.

V. RUTHENIUM. In the variety of conditions of oxidation in which they are found, the compounds of ruthenium resemble those of osmium. The lowest three oxides are basic in character, (RuO; Ru_2O_3; RuO_2), and form salts of which the three chlorides, ($RuCl_2$; Ru_2Cl_6; $RuCl_4$), are typical. The trioxide, (RuO_3), is known only in combination, where it acts as an acid and forms salts of the type $\overset{I}{R}_2RuO_4$. Another oxide, (Ru_2O_7), known only in combination, forms salts represented by the formula $\overset{I}{R}RuO_4$. The tetroxide (RuO_4) is volatile and similar to the corresponding oxide of osmium in its chemical behavior; it has a characteristic odor. A solution of the trichloride, (Ru_2Cl_6), throws out, when heated, a dark precipitate which is generally supposed to be an oxychloride; this precipitate is held in suspension in the liquid and gives a pronounced coloration,

even in very dilute solutions. Hydrogen sulphide, acting upon solutions of ruthenium salts, precipitates a mixture of sulphides, oxysulphides, and sulphur; this mixture is brown or black, and may contain one or more of the sulphides Ru_2S_3, RuS_2, and RuS_3.

Estimation. The platinum metals are weighed in the elementary condition, obtained as described under Preparation of the various metals.

Osmium may be determined volumetrically by causing potassium iodide to act upon the tetroxide in the presence of dilute sulphuric acid, ($OsO_4 + 4KI + 2H_2SO_4 = OsO_2 + 2K_2SO_4 + 4I + 2H_2O$), and estimating by means of sodium thiosulphate the iodine thus liberated (Klobbie, Chem. Central-Blatt (1898) II, 65 (abstract).,

Separation. The separation of the platinum metals has been considered under Platinum. The following are additional references: Gibbs, Amer, Jour. Sci. [2] XXXI, 63; XXXIV, 341; XXXVII, 57; Forster, Zeitsch. anal. Chem. V, 117; Bunsen, Liebig Annal. CXLVI, 265; Chem. News XXI, 39; Deville and Debray, Compt. rend. LXXXVII, 441; Chem. News XXXVIII, 188; Wilm, Ber. Dtsch. chem. Ges. XVI, 1524; Leidie, Compt. rend. CXXXI, 888; Bull. Soc. Chim. d. Paris [3] XXVII, 179.

EXPERIMENTAL WORK ON THE PLATINUM METALS.*

Experiment 135. *Precipitation of palladious iodide*, (PdI_2). To a solution of a palladium salt add a little potassium iodide in solution.

Experiment 136. *Precipitation of palladious sulphide*, (PdS). (*a*) Pass hydrogen sulphide through a solution of a palladious salt.

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* For experimental work on platinum see page 129.

(*b*) Try the action of ammonium sulphide upon a palladious salt in solution.

Experiment 137. *Precipitation of elementary palladium.* To a solution of a palladium salt add sodium carbonate to alkaline reaction; add also a few drops of alcohol and boil.

Experiment 138. *Action of nitric acid upon palladium.* Try the action of nitric acid upon a small piece of metallic palladium.

Experiment 139. *Precipitation of osmium sulphide,* (OsS_4). (*a*) To a solution of osmium tetroxide acidified with hydrochloric acid add a little hydrogen sulphide.

(*b*) Try the action of ammonium sulphide upon the tetroxide in solution.

Experiment 140. *Formation of potassium osmate,* (K_2OsO_4). To a solution of osmium tetroxide add a solution of potassium hydroxide. Note the yellow color.

Experiment 141. *Action of reducing agents upon osmium tetroxide.* Try the action of an alkali sulphite, formic acid, and tannic acid, respectively, upon a solution of osmium tetroxide.

Experiment 142. *Action of osmium tetroxide upon hydriodic acid.* To a solution of osmium tetroxide add a little starch paste and a small crystal of potassium iodide. Acidify the solution with dilute sulphuric acid. Note the blue color, due to free iodine.

Experiment 143. *Precipitation of elementary osmium.* (*a*) To a solution of the tetroxide add stannous chloride.

(*b*) Try the action of zinc and hydrochloric acid upon a solution of the tetroxide.

Experiment 144. *Odor test for osmium.* Warm a dilute solution of osmium tetroxide, or warm with nitric acid a solution of any osmium salt of the lower condition of oxidation. Note the odor.

Experiment 145. *Precipitation of iridium sulphide,*

(Ir_2S_3). Pass hydrogen sulphide through a solution of iridium tetrachloride. Try the action of ammonium sulphide upon the precipitate.

Experiment 146. *Formation of the double chlorides of iridium with ammonium and potassium*, ($(NH_4)_2IrCl_6$ and K_2IrCl_6). To separate portions of a fairly concentrated solution of iridium tetrachloride add ammonium chloride and potassium chloride respectively.

Experiment 147. *Reduction of iridium salts.* (*a*) To a solution of iridium tetrachloride add oxalic acid.

(*b*) Try similarly the action of zinc upon an acid solution of the salt.

Experiment 148. *Action of sodium hydroxide upon iridium tetrachloride.* Add sodium hydroxide in excess to iridium tetrachloride and warm. Note the change in color. The iridium salt is said to be reduced to the trichloride by this treatment. Acidify with hydrochloric acid and add potassium chloride. Note the absence of precipitation.

Experiment 149. *Precipitation of rhodium sulphide*, (Rh_2S_3). Pass hydrogen sulphide through a solution of sodium-rhodium chloride. Try the action of ammonium sulphide upon the sulphide precipitated.

Experiment 150. *Reduction of rhodium salts.* To an acid solution of a rhodium salt add zinc.

Experiment 151. *Formation of the double nitrite of potassium and rhodium*, ($K_3Rh(NO_2)_6$). To a solution of sodium-rhodium chloride add potassium nitrite in solution and warm. Try the action of hydrochloric acid upon the precipitate.

Experiment 152. *Precipitation of rhodium hydroxide*, ($Rh(OH)_3$). Note the first action and the action in excess of sodium or potassium hydroxide upon a solution of sodium-rhodium chloride. Boil the solution just obtained.

Experiment 153. *Precipitation of ruthenium sulphide*,

(Ru_2S_3). (*a*) To a solution of ruthenium trichloride add hydrogen sulphide.

(*b*) Use ammonium sulphide as the precipitant.

Experiment 154. *Formation of the soluble double nitrite of ruthenium and potassium*, ($K_3Ru(NO_2)_6$). To a solution of ruthenium trichloride add a solution of potassium nitrite. Note the color. Add ammonium sulphide to the solution.

Experiment 155. *Precipitation of ruthenium hydroxide*, ($Ru(OH)_3$). To a solution of ruthenium trichloride add sodium or potassium hydroxide in solution.

Experiment 156. *Precipitation of metallic ruthenium.* To an acid solution of a ruthenium salt add metallic zinc.

GOLD, Au, 197.2.

Discovery. Gold is probably one of the earliest known of the metals. In very ancient records frequent mention is made of its uses. As far back as 3600 B.C. in the Egyptian code of Menes a ratio of value between gold and silver (2.5 : 1) is mentioned. Rock carvings of Upper Egypt dating from 2500 B.C. show crude representations of the washing of gold-bearing sands in stone basins, and of the melting of the metal in simple furnaces by means of mouth blowpipes. In fact the discovery of gold dates back to the beginnings of civilization. The search for it furnished the motive of many voyages of discovery and conquest, which resulted in the extension of civilization; and from the desire to change the base metals into gold sprang the study of alchemy, from which developed the science of chemistry.

Occurrence. Gold occurs in nature both free and in combination. Free or native gold is found (1) as vein gold, in the quartz veins which intersect metamorphic rocks, and (2) as placer gold, generally in the form of grains or nuggets, in alluvial deposits of streams. Native gold is

usually alloyed with silver, which sometimes amounts to as much as fifteen per cent. of the alloy. Iron and copper are sometimes present, and bismuth, palladium, and rhodium alloys are known.

In combination gold is found as follows:

Petzite, $(AgAu)_2Te$,	contains	18–24% Au
Sylvanite, $(AuAg)Te_2$,	"	26–29% "
Goldschmidtite, Au_2AgTe_6,	"	31–32% "
Krennerite, $(Au,Ag)Te_2 \cdot AuTe_2$,	"	30–34% "
Calaverite, $(Au,Ag\ Te_2 \cdot AuTe_2$,	"	38–42% "
Kalgoorlite, $HgAu_2Ag_6Te_6$,	"	20–21% "
Nagyagite, $Au_2Pb_{14}Sb_3Te_7S_{17}$,	"	5–12% "

Extraction. The six processes indicated below follow the principal methods that have been employed for the extraction of gold.

(1) *Washing or Hydraulicking.* This method is applied mainly to placer deposits. Powerful jets of water are directed upon the gold-bearing sands, causing them to pass through a series of sluices. Because of its higher specific gravity the gold is largely left behind, while the other materials are carried away.

(2) *Amalgamation (primitive).* In this process the crushed ore or the gold-bearing sand is first washed, to remove the greater part of the light, worthless material, and the remainder is rubbed with mercury in a mortar. The amalgam thus obtained is heated, whereupon the mercury is volatilized and the gold remains.

(3) *Stamp battery amalgamation.* The ore is pulverized and mixed with water, and in the form of pulp caused to pass over a series of amalgamated copper plates. Gold amalgam forms on the plates, and from time to time it is removed and cupelled.

(4) *Chlorination.* (*a*) Vat process. The crushed ore is placed loosely in large vats and moistened with water.

Chlorine is forced in, and the whole is allowed to stand for about twenty-four hours. The material is then leached with water until the washings give no further test for gold. The solution of gold chloride thus obtained is treated with sulphur dioxide, to destroy the excess of chlorine, and then with hydrogen sulphide. The gold sulphide thus precipitated is decomposed with borax and the gold is melted into bullion.

(*b*) Barrel process. Into large barrels are put water and sulphuric acid, the ore, and chloride of lime. The barrels are then closed and rotated for a period varying from one hour to four hours. At the end of that time the contents are leached and the gold is extracted as described above.

The chlorination process is generally applied to low-grade ores, and these must have been roasted unless the gold occurs in them native.

(5) *Cyanide process.* The ore, ground fine, is placed in large vats, and a dilute solution (.2–.5%) of potassium cyanide is forced in. After a time the solution is drawn off and passed over zinc shavings, upon which the gold is deposited as a black slime. The mixture of zinc and gold is either treated with sulphuric acid, to dissolve the zinc, or roasted with a flux of niter and carbonate of soda. The reactions which take place in the cyanide process may be represented as follows:

(1) $4Au + 8KCN + O_2 + 2H_2O = 4KAu(CN)_2 + 4KOH.$

(2) $2KAu(CN)_2 + 2Zn + 2H_2O =$
$2KOH + H_2 + 2Zn(CN)_2 + 2Au.$

(6) *Smelting.* In smelting the gold ore is mixed with some other metallic ore appropriately chosen, and the mixture is subjected to intense heat. The gold alloys with the other metal, and the alloy is separated from the residue, or slag, and worked for gold. Three modifications

of this important process are in common use, viz., lead, copper matte, and iron matte smelting. The process of lead-smelting is in outline as follows: The alloy obtained by heating a mixture of gold and lead ores is melted with zinc. The gold and silver combine with the zinc and rise to the surface, leaving the lead below. The alloy of gold, silver, and zinc is then skimmed off and roasted. The zinc passes off, leaving the gold and silver, which are separated by electrolysis.

The Element. *A. Preparation.* As extracted from its ores gold is in the elementary condition (*vid.* Extraction).

B. Properties. Of a characteristic yellow color, gold is the most malleable and ductile of the metals. It is about as soft as silver. It is insoluble in acids, but is attacked by aqua regia, chlorine, bromine, and potassium cyanide. Its melting-point is 1037° C.,—just above that of copper. Gold alloys with nearly all the metals. It is occasionally found crystallized in the cubic system. It is a good conductor of heat and electricity. Its specific gravity is 19.49.

Compounds. *A. Typical forms.* The following compounds of gold may be considered typical forms:

Oxides..........	Au_2O	Au_2O_2	Au_2O_3
Hydroxide......			$Au(OH)_3$
Chlorides.........	$AuCl$	Au_2Cl_4	$AuCl_3$
Double chlorides, many of the types			$AuCl_3 \cdot \overset{I}{R}Cl$
			$AuCl_3 \cdot \overset{II}{R}Cl_2$
Bromides........	$AuBr$	Au_2Br_4	$AuBr_3$
Double bromides, of the type.....			$AuBr_3 \cdot \overset{I}{R}Br$
Iodides.........	AuI		AuI_3
Double iodides, of the type.			$AuI_3 \cdot \overset{I}{R}I$
Sulphides.......	Au_2S	Au_2S_2	Au_2S_3
			$2Au_2S_3 \cdot 5Ag_2S$
Double sulphides..	$Au_2S \cdot Na_2S$		$2Au_2S_3 \cdot 3MoS_2$
			$Au_2S_3 \cdot 3MoS_4$

Sulphites (double)	$Au_2SO_3 \cdot 3Na_2SO_3 + 3H_2O$	$Au_2(SO_3)_3 \cdot 5K_2SO_3 + 5H_2O$
Sulphates........	$AuSO_4$	$Au_2(SO_4)_3 \cdot K_2SO_4$
Nitrate..........		$Au(NO_3)_3 \cdot HNO_3$
Cyanides.........	$AuCN$	$Au(CN)_3$
Double cyanides..	$AuCN \cdot KCN$	$Au(CN)_3 \cdot KCN$, etc.
Sulphocyanides...	$AuCNS \cdot KCNS$	$Au(CNS)_3 \cdot KCNS$

B. Characteristics. The compounds of gold are known chiefly in two conditions of oxidation, of which aurous oxide, (Au_2O), and auric oxide, (Au_2O_3), serve as types. When metallic gold is dissolved in aqua regia auric chloride is formed, a yellow crystalline salt soluble in water; when auric chloride is heated to 180° C. it goes over to aurous chloride, a white powder insoluble in water. The aurous salts resemble the salts of silver and of copper in the cuprous condition; the auric salts resemble those of aluminum and of iron in the ferric condition. The auric hydroxide, ($Au(OH)_3$), is acidic in character and unites with bases to form aurates of the type $\overset{I}{R}AuO_2$. Hydrogen sulphide precipitates brownish-black auric sulphide, (Au_2S_3 or $Au_2S_2 + S$), from cold solutions of gold salts, and steel-gray aurous sulphide, (Au_2S or $Au_2S + S$), from hot solutions. Salts of gold in solution are easily reduced to the metal by reducing agents.

Estimation. *A. Gravimetric.* Gold is weighed as the metal. From solutions it is precipitated by reducing agents, such as ferrous sulphate, oxalic acid, formaldehyde, and hydrogen dioxide in alkaline solution.

B. Volumetric. Gold may be determined volumetrically (1) by allowing potassium iodide to act upon auric chloride, ($AuCl_3 + 3KI = 3KCl + AuI + I_2$), and estimating the iodine thus freed by means of thiosulphate (Peterson, Zeitsch. anorg. Chem. XIX, 63; Gooch and Morley, Amer. Jour. Sci. [4] VIII, 261; Maxson, Amer. Jour. Sci. [4] XVI); (2) by warming a solution of auric chloride with a measured amount of arsenious acid solution which must be in ex-

cess, ($3As_2O_3 + 4AuCl_3 + 6H_2O = 3As_2O_5 + 12HCl + 4Au$), and determining the excess of arsenious acid by iodine in the usual way (Rupp, Ber. Dtsch. chem. Ges. xxxv, 2011; Maxson, *loc. cit.*).

Separation. Gold and platinum fall into the analytical group of arsenic, antimony, and tin. From these they may be separated by the following process: fusion of the sulphides with sodium carbonate and niter, and removal of the arsenic by extraction with water; treatment of the insoluble residue with zinc and hydrochloric acid, which reduces the tin and antimony to the metallic condition; boiling with hydrochloric acid, which dissolves the tin; then with nitric and tartaric acids, which dissolves the antimony, leaving gold and platinum.

For the separation of gold from platinum and the platinum metals *vid.* Platinum.

EXPERIMENTAL WORK ON GOLD.

Experiment 157. *Extraction of gold from its ores.* (*a*) Digest for several hours in a beaker on a steam-bath about 100 grm. of finely ground gold ore with a dilute solution of potassium cyanide, adding water from time to time to replace the liquid evaporated. Filter, pass the filtrate several times through a funnel containing zinc shavings, until upon testing the liquid with a fresh piece of zinc no discoloration of the metal is observed. Dissolve the zinc in hydrochloric acid to remove the black deposit. Filter, dissolve the residue in aqua regia, remove the excess of acid by evaporation, and test for gold by stannous chloride, ferrous sulphate, etc.

(*b*) Mix in a glass-stoppered bottle about 100 grm. of finely ground "oxidized" or previously roasted ore with a little bleaching salt and enough water to give the mass the consistency of thin paste. Then add gradually enough sulphuric acid to start an evolution of chlorine. Close the

bottle and shake it, to insure a thorough mixing of the contents. Allow the action to go on for several hours, agitating the mass occasionally, and taking care to have an excess of chlorine present throughout the process. Extract with water, concentrate if necessary, and test for gold in the solution. A two per cent. solution of bromine may be substituted for the materials generating chlorine.

Experiment 158. *Precipitation of the sulphide of gold,* (Au_2S_3 or Au_2S_2+S?). Into a cold solution of auric chloride pass hydrogen sulphide. Try the action of yellow ammonium sulphide upon the precipitate.

Experiment 159. *Formation of aurous iodide,* (AuI). To a solution of auric chloride add a few drops of a dilute solution of potassium iodide. Note the precipitate, and the solvent action of an excess of the reagent.

Experiment 160. *Formation of ammonia aurate, "fulminating gold,"* ($(NH_3)_2Au_2O_3$). To a very dilute solution of a salt of gold add a little ammonium hydroxide.

CAUTION. Do not attempt to isolate the precipitate. Note that neither potassium nor sodium hydroxide gives a precipitate under similar conditions of dilution.

Experiment 161. *Formation of the "purple of Cassius."* To a very dilute solution of a gold salt add a drop or two of dilute stannous chloride solution.

Experiment 162. *Precipitation of gold.* To separate portions of a solution of a gold salt add ferrous sulphate and oxalic acid in solution. Observe the color by transmitted light.

Experiment 163. *Solvent action of certain reagents upon gold.* Try separately upon metallic gold the action of aqua regia, chlorine or bromine water, and a dilute solution of potassium cyanide.

THE NEWLY DISCOVERED GASES OF THE ATMOSPHERE.

Argon, A, 39.9 Krypton, Kr, 81.8
Helium, He, 4 Neon, Ne, 20
Xenon, X, 128

Discovery. In 1892 Lord Rayleigh, while engaged in the study of the density of elementary gases, made the important observation that the nitrogen obtained from nitric acid or ammonia was about one half of one per cent. lighter than atmospheric nitrogen (Proc. Royal Soc. LV, 340). An investigation of this difference led to the discovery two years later of the gas Argon (ἀργός, *inert*) by Lord Rayleigh and Professor William Ramsay (Proc. Royal Soc. LVII, 265; Amer. Chem. Jour. XVII, 225). An experiment made by Cavendish in 1785 seems also to have resulted in the separation of this gas (Phil. Trans. Roy. Soc. (1785) LXXV, 372, and (1788) LXXVIII, 271).

In the course of analytical work on uraninite undertaken by Hillebrand in 1888, a gas which he thought to be nitrogen was obtained upon the boiling of the mineral with dilute sulphuric acid (Bull. U. S. Geol. Sur. No. 78, p. 43; Amer. Jour. Sci. [3] XL, 384). In 1895 Ramsay, whose attention had been called to Hillebrand's work, and who doubted whether nitrogen could be obtained by the method described, prepared some of the gas by Hillebrand's process from cleveite, a variety of uraninite. He then sparked the gas with oxygen over soda to remove the nitrogen. Observing very little contraction, he removed the excess of oxygen by absorption with potassium pyrogallate and examined the residual gas spectroscopically. The spectrum showed argon and hydrogen lines, and in addition a brilliant yellow line, (D_3), coincident with the helium line

of the solar chromosphere discovered by Lockyer in 1868 (Proc. Royal Soc. LVIII, 65, 81). The only previous note regarding helium as a terrestrial element is a statement by Palmieri, in 1881, that a substance ejected from Vesuvius showed the line D_3 (Rend. Acc. di Napoli XX, 233); he failed to describe his treatment of the material, however, and he seems to have made no further investigation of the subject. Kayser first detected helium in the atmosphere, in 1895 (Chem. News LXXII, 89), several months after Ramsay's discovery.

The year 1898 witnessed the discovery by Ramsay and Travers of three other inert atmospheric gases. Having allowed all but one seventy-fifth of a given amount of liquid air to evaporate, and having removed the oxygen and nitrogen remaining by sparking over soda, they obtained a small amount of a gas which, while showing a feeble spectrum of argon, gave new lines as well. This newly discovered gas they named Krypton, from κρυπτός, *hidden* (Proc. Royal Soc. LXIII, 405).

By fractioning the residue after the evaporation of a large amount of liquid air they found evidence of a gas of greater density than krypton, and for this heavy gaseous element the name Xenon (*ξένος, stranger*) was chosen (Chem. News LXXVIII, 154).

The third discovery of the year by the same investigators was that of Neon (*νέος, new*), a gas of less density than argon. The first fraction obtained from the evaporation of liquid air was mixed with oxygen and sparked over soda, and the excess of oxygen was removed by phosphorus. The remaining gas yielded a new and characteristic spectrum (Proc. Royal Soc. LXIII, 437).

Occurrence. Argon forms about one per cent. of the air by volume. It is found in small quantities in gases from certain mineral springs, e.g. Bath, Cauterets, Wildbad, Vöslau, the sulphur spring of Harrogate; also in the gases

occluded in rock salt. It has been detected in some helium-bearing minerals, e.g. cleveite, bröggerite, uraninite, and malacon.

Helium, the existence of which was first observed in the sun, occurs in very small proportion in the terrestrial atmosphere. The chief sources of the gas have been certain rare minerals, among which are uraninite (pitch-blende), cleveite, monazite, fergusonite, samarskite, columbite, and malacon. It has been found also in some mineral springs, e.g. Bath, Cauterets, and Adano, near Padua.

The other gases of this group are present in the air in very minute quantities. Neon is said to constitute 0.0025% and krypton 0.00002% of the atmosphere. Traces of neon have been detected in the helium from the springs of Bath.

Extraction. Argon, contaminated with a greater or less percentage of the associated gases, may be extracted by the following methods:

(1) *From atmospheric nitrogen.* The nitrogen is passed over red-hot magnesium filings; a nitride is thus formed, while the argon is left uncombined (Ramsay). Heated lithium may be substituted for magnesium.

(2) *From air.* Induction sparks are passed through a mixture of oxygen and air contained in a vessel which is inverted over caustic potash. The oxygen and nitrogen combine and dissolve in the potassium hydroxide, leaving the argon (Rayleigh).

Helium may be obtained from its mineral sources by boiling the material with dilute sulphuric acid, or by heating *in vacuo.*

Krypton and xenon are extracted as follows: After the evaporation of a large amount of liquid air the residue is freed from oxygen and nitrogen and liquefied by the immersion of the containing vessel in liquid air. The greater part of the argon can be removed as soon as the temperature rises. By repetitions of this process the

three gases can be separated from one another, krypton exercising much greater vapor pressure than xenon at the temperature of boiling air (Ramsay and Travers, Proc. Royal Soc. LXVII, 330).

Neon is obtained from the gas, largely nitrogen, that first evaporates from liquid air. This gas is liquefied, and a current of air is blown through it. The material that first evaporates is passed over red-hot copper, to remove the oxygen, and after being freed from nitrogen in the usual manner, is liquefied. By fractional distillation helium and neon are removed, and argon is left behind. By the use of liquefied hydrogen helium and neon are separated, as neon is liquefied or solidified at the temperature of boiling hydrogen, while helium remains gaseous. Several fractionations are necessary to obtain pure neon (Ramsay and Travers, Proc. Royal Soc. LXVII, 330).

Properties. The newly discovered constituents of the atmosphere are inert, colorless, probably monatomic gases, which have not been known to form definite compounds.

Argon is somewhat soluble * in water. Its density is 19.96 and its specific heat 1.645. It solidifies at $-191°$ C., melts at $-189.5°$ C., and boils at $-185°$ C. Argon gives two distinct spectra, according to the strength of the induction current employed and the degree of exhaustion in the tube. When the pressure of the argon is 3 mm. the discharge is orange-red and the spectrum shows two particularly prominent red lines. If the pressure is further reduced, and a Leyden jar is intercalated in the circuit, the discharge becomes steel-blue and the spectrum shows a different set of lines (Crookes, Amer. Chem. Jour. XVII, 251).

Helium is slightly soluble † in water. Its density is 1.98. Its spectrum is characterized by five brilliant lines,—

* 100 volumes of water will dissolve 3.7 volumes of argon at 20° C.

† 100 volumes of water will dissolve about 1.4 volumes of helium at 20° C.

one each in the red, yellow, blue-green, blue, and violet. Reference has already been made to the yellow line D_3.

Krypton is less volatile than argon. Its density is 40.78. Its spectrum is characterized by a bright line in the yellow and one in the green.

Xenon also is less volatile than argon, and it has a much higher boiling-point. Its density is 64. Its spectrum is similar in character to that of argon, though the position of the lines is different. With the ordinary discharge the glow in the tube is blue and the spectrum shows three red and about five brilliant blue lines. With the jar and spark-gap the glow changes to green and the spectrum is characterized by four green lines (Ramsay and Travers, Chem. News LXXVIII, 155).

Neon is more volatile than argon. Its density is 9.96. Its spectrum is characterized by bright lines in the red, orange, and yellow, and faint lines in the blue and violet.

RECENT UNCONFIRMED DISCOVERIES.

In September, 1896, Barrière announced the discovery in monazite sands of an unknown element which differed from the members of the cerium group and from thorium and zirconium in forming no double sulphate with either sodium or potassium sulphate, and from the members of the yttrium group in being precipitable by sodium thiosulphate. He gave as the approximate atomic weight of the element 104, and proposed for it the name Lucium (Chem. News LXXIV, 159). A few weeks later Crookes examined some of Barrière's material, and declared lucium to be yttrium with some admixture of erbium, didymium, and ytterbium (Chem. News LXXIV, 259). The following year Shapleigh confirmed Crookes's results, and pointed out the weak places in Barrière's deductions (Chem. News LXXVI, 41).

In 1897 Chruschtschoff called attention to a new member of the didymium group which he distinguished from praseo- and neodymium by the blue color of its salts. The spectrum was in part that of neodymium. He suggested the name Glaukodymium (γλαυκός, *blue-gray*) (Jour. Rus. Phys. Chem. Soc. XXIX, 206). Although it is considered quite possible that praseo- and neodymium are not simple bodies, no confirmation of Chruschtschoff's discovery has appeared.

Nasini, Anderlini, and Salvadori, in 1898, discovered in the spectra of gases from the Solfatara di Pozzuoli and the fumaroles of Vesuvius a line (1474 K) of the corona never before observed in terrestrial matter. They called the unknown gas the presence of which was thus indicated Coronium (Atti R. Accad. dei Lincei, Roma [5] VII, II, 73; Amer. Chem. Jour. XX, 698).

The same year Brush, while studying the relation of pressure to the heat conductivity of gases, extracted from glass a gaseous substance which seemed to be different from all known gases. He concluded that its heat conductivity was 100 if H = 1; its density, also referred to hydrogen as the standard, was 0.0001, and its molecular weight 0.0002. He suggested that it might be the ether of the physicist, and proposed for it the name Etherion (Amer. Chem. Jour. XX, 873; Chem. News LXXVIII, 197). Crookes, upon examination of the evidence given by Brush, pronounced the gas probably water vapor (Chem. News LXXVIII, 221).

About the time that Ramsay and Travers announced the discovery of krypton and neon in 1898, they first mentioned Metargon (Proc. Royal Soc. LXIII, 437). It was obtained in the liquefaction of large quantities of argon, remaining in the form of a white solid after the liquid had largely boiled away. The gas obtained from this solid had a density close to that of argon; its spectrum

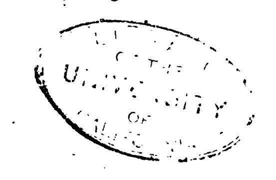
resembled that of argon and also that of carbon. Two years later the same investigators announced that this gas was merely argon mixed with some compounds of carbon (Proc. Royal Soc. LXVII, 329).

Crookes, in 1899, stated that as the result of a long series of fractional fusions, crystallizations, and precipitations of salts obtained from yttrium earth, he had discovered an element which he had named Monium. A little later, in recognition of the Queen's jubilee, he changed the name to Victorium (Proc. Royal Soc. LXV, 237). The new element was described by him as having a pale-brown color, as being less basic than yttrium, as being easily soluble in acids, and as forming with potassium sulphate a double sulphate less soluble than the corresponding salt of yttrium, and more soluble than the corresponding salts of the cerium group. Assuming the oxide to be Vc_2O_3, he calculated the atomic weight as 117.

Previous to 1898 the presence of "radiant matter" in uranium and thorium minerals, particularly in pitchblende, had frequently been noticed, and investigations of the phenomenon had been carried on. It is not yet fully determined whether the actinism is due to the presence in these minerals of certain elements having distinct radioactive properties, though three substances possessing this quality, and differing in other characteristics, have been isolated and described as compounds of newly discovered elements. In 1898 P. and C. Curie announced the discovery in pitch-blende of Polonium (*Polonia, Poland*), and the next year, together with Bemont, of another element, Radium* (Compt. rend. CXXVII, 175, 1215). Also in 1899 Debierne named Actinium as a third radioactive element (Compt. rend. CXXX, 906).

* Recent work on this interesting substance has led many chemists to assign radium a place among the elements. See Mme. Curie, Compt. rend. CXXXV, 161; Runge and Precht, Annal. der Phys. u. Chem. [4] X, 655; Hammer, Chem. News LXXXVII, 25.

In the summer of 1901 Baskerville described some work on pure thorium salts which had suggested to him the probable existence of an unknown element associated with thorium. He found it possible, by fractioning pure thorium dioxide, to obtain two oxides of specific gravity 9.25 and 10.53 respectively. Radioactivity increased with specific gravity, the oxide of lower specific gravity being practically inactive. A determination of the atomic weight of thorium from the pure tetrachloride gave 223.25, as against 232.5, the generally accepted value. The probable atomic weight of the new element was given as between 260 and 280, and the name proposed for it was Carolinium, because the thorium salts were prepared from the monazite sands of the Carolinas (Jour. Amer. Chem. Soc. XXIII, 761).



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